

Biofuels from Kraft Black Liquor  
*Pilot-Scale Gasification Development and  
Techno-Economic Evaluation of Industrially  
Relevant Biofuel Production Pathways*

Yawer Jafri

Energy Engineering

Doctoral Thesis

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## Abstract

Forest residues and by-products such as black liquor (BL) and harvesting residues are viewed as strategically important feedstock for the production of biofuels in countries with extensive forest-based industries. Upgrading BL to biofuels can not only contribute to the reduction of transport greenhouse gas (GHG) emissions but potentially also help pulp mills expand their pulp production capacity and product base. Two conversion routes are seen as industrially relevant in the short-to-medium term: (a) gasification-catalytic synthesis, (b) separation-hydrotreatment.

The production of methanol and dimethyl ether from kraft BL in an entrained-flow gasifier referred to as the BLG concept has been demonstrated extensively in pilot scale, although a complete analysis of technical performance based on experimental measurements has not been performed previously. A limitation of BL is that it is not transportable. The production potential of a BL-based, mill-integrated biofuel plant is effectively constrained by the pulp throughput at the mill, which also places a restriction on achievable economies-of-scale. An advantage of BL is that it is rich in catalytically active sodium compounds that help achieve efficient conversion during BLG. The catalytic effect of these compounds can be utilized to increase biofuel production potentials, and potentially also improve economic performance, by blending BL with similar but more energy-dense forest-based residual feedstocks such as pyrolysis oil (PO). Several commercial actors are currently also testing the technical viability of using the separation-hydrotreatment route for the production of renewable petrol and diesel blendstock from kraft lignin. The initial conversion in both of the aforementioned routes is co-located with a pulp mill. Depending on the desired end product, subsequent upgrading and finishing may be carried out at a pulp mill or a crude oil refinery. The resulting impact on production economics and energetic performance is complex and little studied.

The main aim of this thesis is to evaluate the technical and economic viability of kraft BL-based biofuel production pathways that are adjudged to be industrially relevant, that is they are seen as commercially deployable in the short-to-medium term at the present time. Detailed mass and energy balances based on experimental measurements were compiled to fully characterize the gasification performance of unblended BL under various operating conditions. The catalytic co-gasification of PO and BL was studied in pilot-scale experiments to evaluate key performance indicators.

The results indicate that the biofuel production potential of BL can be significantly enhanced through co-gasification without compromising the possibility of successful mill integration. Blending BL with up to 20 wt.% PO resulted in a notable improvement in syngas quality. The carbon conversion efficiency of PO/BL blends was similar to that of unblended BL. There were no signs of an increase in either soot or tar formation. Analyses of gas condensate samples found traces of unknown uncharged forms of sulfur. While sulfur reduction efficiencies were generally high, balance closures for co-gasification could not consistently be obtained owing to analytical

difficulties. Further research on sulfur chemistry and characterization in the BLG process therefore appears warranted.

Pilot-scale entrained-flow gasification experiments are expensive and time consuming. An alternative is thermodynamic equilibrium calculations (TECs), which were found to predict the flows of major syngas and slag constituents with a high degree of accuracy, particularly when known deviations are taken into account. Prediction results were found to be highly sensitive to small variations in feedstock composition. The validation of TEC results with experimental data is recommended as a means of identifying potential deviations and avoiding misattribution of underlying causes.

The results of a profitability evaluation indicate that the production of biofuels from BL can potentially also be viable in relatively small-scale plants (50-100 MW<sub>th</sub>) that may be used to debottleneck capacity constrained recovery boilers. In a case where drop-in biofuels are produced from BL part streams in small-scale plants integrated with a crude oil refinery, the best performing pathways from both of the studied routes were able to return minimum fuel selling prices of ~80 EUR<sub>2017</sub>/MWh. Hence, both the BL gasification route and the lignin separation route represent an economically interesting option for meeting the rising demand for renewable drop-in transport fuels.

While co-gasifying BL and PO or blending syngas from unblended BL with electrolysis hydrogen offer larger biofuel production potentials and a more diverse feedstock base, gasification of unblended BL comes out as the lowest cost option for the production of drop-in biofuels from BL part-streams. In energy market conditions with low electricity prices, modern market pulp mills with a large energy surplus that is exported as electricity are identified the most suitable mill type for co-location and integration of biofuel production. In the lignin separation-hydrotreatment route, the use of natural gas as hydrogen source offers superior economic performance, while the use of electricity under the assumption of a Swedish mix can deliver considerably greater GHG savings.

It is expected the demand for forest-based drop-in petrol and diesel alternatives will continue to grow in face of a sustained legislative push. The results of the work presented in this thesis indicate that the gasification-catalytic synthesis and separation-hydrotreatment routes provide two complementary, strategically interesting options for achieving deep reductions in transport GHG emissions.

## **Author Contribution**

### **Paper I**

Jafri participated in the execution of the experimental runs, gathered process data, analyzed experimental results in collaboration with Kirtania and Furusjö and wrote most of the paper under the supervision of Furusjö and Gebart.

### **Paper II**

Jafri planned the experiments in collaboration with Furusjö, assisted in the execution of the experimental runs, gathered process data, analyzed experimental results and wrote the paper under the supervision of Furusjö and Gebart.

### **Paper III**

Jafri participated in carrying out the thermodynamic equilibrium calculations, analyzed calculation results in collaboration with Furusjö and contributed to the writing of the paper under the supervision of Furusjö.

### **Paper IV**

Jafri developed the material and energy balance models for two of the four routes, carried out the energy performance evaluation and wrote most of the paper under the supervision of Furusjö and Wetterlund.

### **Paper V**

Jafri performed the economic evaluation, evaluated the results and co-wrote the paper under the supervision of Furusjö and Wetterlund.

### **Paper VI**

Jafri developed the material and energy balance models, carried out the energy performance and economic evaluations, evaluated the results and wrote the paper under the supervision of Wetterlund and Furusjö.



## List of Appended Papers

This thesis is based on the following appended papers, which are referred to throughout by their Roman numerals:

### Paper I

Jafri, Y.; Furuşjö, E.; Kirtania, K.; Gebart, R. Performance of a Pilot-Scale Entrained-Flow Black Liquor Gasifier. *Energy & Fuels* 2016 **30** (4), 3175-3185.

DOI: 10.1021/acs.energyfuels.6b00349

### Paper II

Jafri, Y.; Furuşjö, E.; Kirtania, K.; Gebart, R.; Granberg, F. A Study of Black Liquor and Pyrolysis Oil Co-Gasification in Pilot-Scale. *Biomass Conversion and Biorefinery* 2018 **8** (1), 113-124.

DOI: 10.1007/s13399-016-0235-5

### Paper III

Furuşjö, E.; Jafri, Y. Thermodynamic equilibrium analysis of entrained flow gasification of spent pulping liquors. *Biomass Conversion and Biorefinery* 2018 **8** (1), 19-31.

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### Paper IV

Jafri, Y.; Wetterlund, E.; Anheden, M.; Kulander, I.; Håkansson, Å.; Furuşjö, E. Multi-aspect evaluation of integrated forest-based biofuel production pathways: Part 1. product yields & energetic performance. *Energy* 2019 **166**, 401-413.

DOI: 10.1016/j.energy.2018.10.008

### Paper V

Jafri, Y.; Wetterlund, E.; Anheden, M.; Kulander, I.; Håkansson, Å.; Furuşjö, E. Multi-aspect evaluation of integrated forest-based biofuel production pathways: Part 2. economics, GHG emissions, technology maturity and production potentials. *Energy* 2019 **172**, 1312-1328.

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### Paper VI

Jafri, Y.; Wetterlund, E.; Mesfun, S.; Rådborg, H.; Mossberg, J.; Hulteberg, C.; Furuşjö, E. Combining Expansion in Pulp Capacity with Production of Sustainable Biofuels – Techno-economic and GHG Emissions Assessment of Drop-in Fuels from Black Liquor Part-Streams. Manuscript.





## Abbreviations

<b>BL</b>	black liquor
<b>BLG</b>	(entrained-flow) black liquor gasification
<b>BLG-MeOH</b>	methanol from entrained-flow gasification of black liquor
<b>BLG-PTRL</b>	petrol (and LPG) from entrained-flow gasification of black liquor via methanol to gasoline
<b>CAPEX</b>	capital expenditure
<b>CGE</b>	cold gas efficiency
<b>CO-BLG-MeOH</b>	methanol from entrained-flow co-gasification of pyrolysis oil and black liquor
<b>CO-BLG-PTRL</b>	petrol (and LPG) from entrained-flow co-gasification of pyrolysis oil and black liquor
<b>DME</b>	dimethyl ether
<b>DS</b>	dry solids (solids content)
<b>EL-BLG-PTRL</b>	petrol (and LPG) from black liquor gasification syngas mixed with electrolysis hydrogen
<b>FOAK</b>	first-of-a-kind
<b>FT</b>	fischer-tropsch
<b>GHG</b>	greenhouse gas
<b>GL</b>	green liquor
<b>HHV</b>	higher heating value
<b>HVO</b>	hydrotreated vegetable oil
<b>ILUC</b>	indirect land-use change
<b>LPG</b>	liquefied petroleum gas
<b>MFSP</b>	minimum fuel selling price
<b>MSL-HDO</b>	diesel and petrol from hydrotreatment of membrane-separated lignin using natural gas hydrogen
<b>MSL-HDO-EL</b>	diesel and petrol from hydrotreatment of membrane-separated lignin using electrolysis hydrogen
<b>MTG</b>	methanol-to-gasoline
<b>NOAK</b>	n <sup>th</sup> -of-a-kind
<b>OP</b>	operating point
<b>PEM</b>	polymer electrolyte membrane (electrolysis)
<b>PO</b>	pyrolysis oil
<b>RB</b>	recovery boiler
<b>RED</b>	renewable energy directive
<b>ROC</b>	relative oxygen content
<b>STL</b>	sulfite thick liquor
<b>TCI</b>	total capital investment
<b>TEA</b>	techno-economic analysis
<b>TEC</b>	thermodynamic equilibrium calculations
<b>TIC</b>	total inorganic carbon
<b>TOC</b>	total organic carbon
<b>TRL</b>	technology readiness level
<b>VGO</b>	vacuum gas oil



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Yawer  
Luleå, September 2019



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# 1 Introduction

*This chapter begins by reviewing the role of biofuels within the transport sector in European Union and Sweden. It continues with a brief introduction to the pulp and paper industry and a perspective on how biofuels and pulp and paper mills can come together. Various routes for the production of biofuels from kraft black liquor are introduced and a survey of the academic literature on their study and evaluation is provided.*

## 1.1 Biofuels in Perspective

Spurred by the immediacy of climate change mitigation [1], the last decade has witnessed a surge of interest in conceptualizing and actualizing the bioeconomy [2]–[7]. The prevailing vision of the bioeconomy is multi-stranded, but there exists a widely shared understanding of common elements [8]. One of these elements is the shift from fossil resources to bio-based resources for the production of both energy and materials. Another is improved resource utilization, which puts emphasis on the transformation of waste and low value side-flows into higher value products. These two elements come together in policy support for integrated production of energy carriers, fuel, goods and chemicals from biomass in biorefineries [9], which are expected to take over the function currently occupied by crude oil refineries [10]–[12].

Biofuels have been referred to as the most visible output of the bioeconomy [11]. Large-scale production of first-generation biofuels such as ethanol and biodiesel from sugar and vegetable oils has been linked to an assortment of sustainability issues, chief among them being land use change impacts [13]–[17]. The resulting fallout has led to a withdrawal of policy support [18]. More recently, particularly in the EU, policy focus has instead shifted to the development of advanced biofuels from waste and residual streams, several of which are generated by forest-based industries [19], [20]. More efficient use of industrial by-products and waste wood is also seen as a means of reducing pressure on forests [21]. Co-location can confer economic and energetic benefits through improved heat integration, co-use of existing process equipment, synergies in transport logistics and more efficient utilization of surplus by-products [22]–[24].

It is in the above context that upgrading residues and by-products from forestry and forest-based industries to biofuels is viewed as a means of reducing greenhouse gas (GHG) emissions in the transport sector while “maximizing the economic value from tree” [25].

### 1.1.1 In the European Union

Fuel combustion in the transport sector, including international aviation, was responsible for 25% of the GHG emissions in the EU-28 in 2017 [26]. With a share of nearly 83%, road transport dominated transport emissions [27]. Unlike in most other sectors of the EU-28 economy, CO<sub>2</sub>

emissions in road transport grew by 24% between 1990 and 2017 [27]. Despite policy efforts to the contrary, the transport sector continues to be dominated by crude oil-derived fuels. The share of renewable sources in the final energy consumption within the transport sector was 7.6% in 2017 [28]. Only a few countries had met, or were on course to meet, the target of a 10% share by 2020 mandated in the original renewable energy directive (RED) [29], [30].

In December 2018, a revised renewable energy directive (RED II) entered into force. RED II requires member states to oblige fuel suppliers to ensure that the share of renewables within the final consumption of energy in transport reaches 14% by 2030 [19]. To qualify for financial support and to be counted towards the RED II target, biofuels must be able to deliver life cycle GHG savings of at least 65% compared to an appropriate fossil reference using the calculation rules provided in RED II [19]. The sustainability criteria for qualification as a compliant biofuel have also been tightened. The share of biofuels produced from food and feed crops in the final consumption of energy within road and rail transport is limited to 7%. Indirect land use change (ILUC) is addressed by placing limits on the amounts of high ILUC-risk biofuels that can be counted towards the RED II transport target. These limits are set to decrease to zero by 2030. A set of criteria for determining whether a biofuel feedstock carries a high ILUC risk or whether it can be certified as low ILUC-risk is defined in a delegated act [31]. RED II also provides a list of approved feedstocks for advanced biofuels in Annex IX, which have their own specific sub-target within the 14% target for transport, and the contribution of which towards transport targets qualifies for double counting (on an energy basis). The Annex IX feedstocks include, among others, wastes and residues from forestry and forest-based industries such as bark, pre-commercial thinnings, pulping liquors, lignin and tall oil [19].

The targets set out in RED II represent legally binding minimum targets. Some member states such as Sweden have transport emission reduction targets that are more ambitious.

### 1.1.2 In Sweden

The Swedish climate policy framework mandates a minimum 70% reduction in GHG emissions from domestic transport, excluding aviation, by 2030 compared to 2010 levels [32], [33]. The overarching target is to reduce net national GHG emissions to zero by 2045 [34]. In the case of road transport, the reduction required is to be achieved through improved fuel efficiency, an increase in electric car share, and a switch from fossil fuels to economically viable biofuels that not only have significant production potentials but can also comply with the sustainability criteria in RED II [19]. An important regulatory instrument for stimulating the reduction of transport emissions is the reduction obligation scheme (*reduktionsplikt*) [35]. Suppliers of transport fuels are obliged to reduce their GHG footprints by increasing the share of biofuel blends in the petrol and diesel pools by a certain amount each year [36], [37]. The reduction obligation scheme does not cover pure or high-blend biofuels, which are regulated by a separate tax exemption regime [35].

The transport fuels delivered to the Swedish market in 2018 amounted to 91.7 TWh, with diesel and petrol accounting for 60% and 30% of the total, respectively [38]. The share of biofuels was 23%. Recent years have seen a sharp rise in the use of hydrotreated vegetable oil (HVO) as a diesel blending component. In 2018, 17% of the diesel delivered to the Swedish market originated as HVO and an additional 5.5% as fatty acid methyl esters (FAME). A pure HVO variant sold under the commercial name of HVO100 as an alternative to diesel had a transport market share of 4.6%. In contrast to the case of diesel, the share of biofuel blends in petrol was limited to 3%. It is technically possible to blend in greater amounts but the bio-based petrol alternatives currently available on the market are not considered suitable on account of too low octane rating [38]. The high blend ethanol variant E85 had a transport market share that lay below 0.5%.

The majority of the HVO sold on the Swedish market is produced from feedstock sources harvested outside the European Union [38]. In 2018, the most important HVO feedstocks in descending order were palm fatty acid distillate, slaughterhouse waste oil and raw tall oil with market shares of 46%, 37% and 10%, respectively. Palm fatty acid distillate was recently stripped of its advantageous classification as a residue in Sweden whereby it would no longer be able to meet future sustainability criteria without certification [39], [40]. Raw tall oil is a by-product of pulp making. The maximum theoretical production potential of Swedish raw tall oil-based diesel is estimated to be 1.75 TWh, or less than 15% of the HVO available on the market [41]. Internationally, significant quantities are used for the manufacture of pine chemicals, which not only limits the amounts available for biofuel production but may also represent a comparably sustainable use of a bio-based resource [42]. Data from 2018 shows that 84% of the ethanol used in the transport sector was produced from maize and wheat, while nearly all of the fatty acid methyl ester was produced from rapeseed oil. As food and feed crops, these feedstocks are allocated a limited role in EU transport emissions policy, as noted in Chapter 1.1.1.

Quotas for drop-in diesel and petrol under the reduction obligation scheme are set to increase in the future, while the current feedstock base is subject to concerns about limited biofuel potentials and sustainability, as discussed above. The absence of economically competitive, GHG emissions-compliant drop-in blending components in significant quantities has recently been highlighted [39]. The production of biofuel blends from forestry residue and forest industry by-products therefore offers a promising route for replacing existing sources and meeting future growth required for the fulfillment of medium and long-term emission reduction targets.

## 1.2 Pulp & Paper Industry in Perspective

Pulping methods can be classified into three principle types: mechanical, chemical and semi-chemical. The most common method is chemical pulping, which was estimated to account for 73% of the wood pulp produced worldwide in 2017-2018 [43]. The predominant chemical pulping process is the kraft process, which had a global market share of 98% in 2017-2018 [43].

Statistics collected by the Confederation of European Paper Industries show that the total production of pulp and paper & board in member countries remained relatively stable at 36-38 Mtons and 90 Mtons, respectively, between 2010 and 2016 [44]. However, the aggregate figures hide some important segmental differences. The rapid expansion of digital media in the last decade has meant that the production of newsprint and other graphic papers in member states has gone down from 45 Mtons to 36 Mtons [44]. However, the production of paperboard, tissue and to a somewhat lesser extent market pulp, has risen in response to growth in the global packaging sector.

### **1.2.1 Kraft Pulping & Black Liquor**

The kraft process can be used to pulp a wide variety of wood types. It uses an alkaline solution of cooking chemicals, principally sodium sulfide and sodium hydroxide, to dissolve some of the hemicelluloses and most of the lignin in the wood. The resulting pulp is comprised of relatively unconverted cellulose fibers, characterized by their superior mechanical strength [45]. Depending mainly on the composition of the wood used, pulp yields can vary between 45-55 wt.% for bleachable-grade hardwood pulps and 40-60 wt.% for softwood pulps [46].

Spent cooking chemicals and dissolved organics are separated from pulp during washing. The resulting complex mixture of water, dissolved organic components and residual cooking chemicals is known as black liquor (BL). Dark in appearance and viscous in consistency, concentrated BL from a modern kraft pulp mill typically has a dry solids (DS) content of 80 to 85% by weight.

An important part of the kraft process and central to its widespread adoption is the recycling of the cooking chemicals used for cooking wood. The cooking chemicals are recovered by combusting BL in a special boiler known as the recovery boiler (RB) and returning the dissolved smelt back to the mill for further processing. The heat recovered from the combustion of the organic fraction in BL is used to generate steam for use in various mill processes and for electricity generation.

### **1.2.2 Pulp & Paper Mills & Biorefining**

It has been argued variously that embracing the biorefinery model can help mills see off medium to long-term strategic challenges such as an intensification of competition in certain market segments and a global trend towards increased digitalization [47]. At the same time, the diffusion of forest biorefineries in the pulp and paper industry has been very slow [48], [49]. Concepts and technologies that have been successfully demonstrated in pilot facilities have, in general, failed to make it across the so-called “valley of death” to widespread commercial deployment [50]. Research in the field of technology innovation systems has shown that adoption of emerging technologies depends not only on technological breakthroughs but financial, organizational, conceptual and structural barriers, such as low fossil prices, divergent political, cognitive and social lock-in and lack of long-term policy support [48], [50].

In addition, market formation is also weak, both because of the need to compete with fossil fuels and because of internal competition from alternative use of raw materials [51] as well as from alternative investments in incumbent technologies [52]. Testing in industrially relevant scales is seen as a requirement for mitigating the technical risk. At the same time, the high cost of full-scale first-of-a-kind (FOAK) biorefinery investments poses a significant barrier to demonstration and commercialization [53], [54]. Thus, large investments in e.g. pulp and paper-based biorefineries are blocked or postponed due to incompatibility with prevalent business models in the industry, resulting in what can be described as a systemic lock-in [52]. In response to calls for change and transformation, it has been found that companies are starting to respond by reviewing their business models, diversifying their product portfolios to include new forest biomass-based products [55] and, in general, “seeking renewal under the emerging concept of bioeconomy” [11].

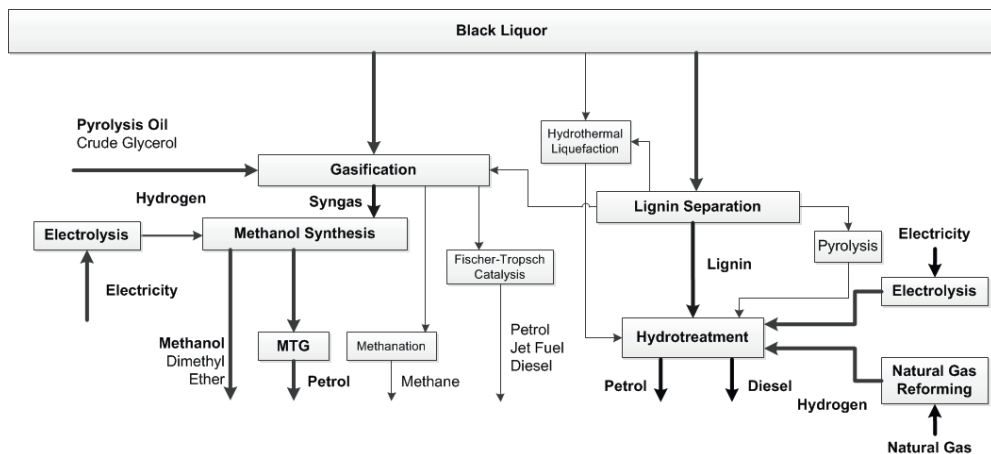
Modern market pulp mills typically produce more steam than is required to meet their own needs [56] and could choose to export their energy surplus in the form of transport biofuels if doing so were deemed sufficiently economically attractive. In Sweden, following recent shifts in climate policy, specifically the launch of the reduction obligation scheme, there are signs that some of the aforementioned structural barriers may be shifting [57]. Since demand prognoses for several pulp and paper segments are rather healthy, mills that wish to expand their pulp production but suffer from limited RB capacity could remove the bottleneck by upgrading some of their BL to biofuels.

### **1.3 Routes for Production of Biofuels from Black Liquor**

Numerous pathways for the production of biofuels and bio-based materials from BL and BL lignin have been proposed and reviewed in the literature [58]–[62]. Figure 1 presents a selection of thermochemical pathways that can be used to produce various biofuels from BL with or without the aid of secondary feedstocks. As may be expected, the level of technology maturity among the proposed alternatives varies significantly. The most well-developed and widely studied pathways can be classified into two thermochemical process routes: (a) gasification-catalytic synthesis, and (b) separation-hydrotreatment.

In the gasification-catalytic synthesis route, BL is gasified under pressure to produce a  $H_2$  and  $CO$ -rich synthesis gas (syngas). Nearly complete carbon conversion is achieved at relatively low temperatures owing to the catalytic effect of the alkali in BL, which also helps suppress the formation of impurities such as tar and soot [63]. The molten slag from the gasifier that contains the cooking chemicals is returned to the mill, while the syngas can be catalytically upgraded to a choice of biofuels and biofuel intermediates, such as methanol, Fischer-Tropsch (FT) liquids and petrol blendstock. Gasification-catalytic synthesis can be used to produce both drop-in and high-blend biofuels.

In the separation-hydrotreatment route, the organic fraction in BL, principally lignin, is separately and upgraded to a transportable intermediate product that can be hydrotreated in a conventional petroleum refinery to produce renewable petrol and diesel blendstock.



**Figure 1. A (non-exhaustive) selection of thermochemical pathways for the production of biofuels from black liquor. The pathways examined in this work, and their constituent feedstocks, intermediates and products, are indicated by thicker arrows and bolded text.**

Biofuels from BL are eligible for double counting towards the transport target in RED II as BL is classed as a forest-based residue (see Chapter 1.1.1). In studying and evaluating different options for producing biofuels from BL, this thesis has chosen to focus on technology tracks seen as “industrially relevant” at the present time. Industrially relevant technology tracks are defined as technology tracks aiming for commercial deployment in the near-term that are undergoing, or have recently undergone, technical demonstration in industrially relevant scales. The focus on technologies deployable in the near future is consistent with the Swedish, and to a lesser extent EU, goal of accelerating the pace of emissions mitigation in transport.

A survey of the pertinent literature and commercial R&D&D initiatives was carried out to identify pathways for evaluation that matched the scope of the thesis, and for which adequate experimental data was available. The production of biofuels from other woody material flows at pulp mills or from forestry residues by either thermochemical or biochemical conversion has not been evaluated except in Papers IV and V where two industrially relevant forest residue-based pathways provide a useful reference point for comparison.

## 1.4 Survey of Existing Research

### 1.4.1 Biofuel Production from Black Liquor

Technology demonstration of the gasification-catalytic synthesis route in industrially relevant scales has been limited to the pressurized oxygen-blown entrained-flow catalytic gasification (BLG) concept originally developed by Chemrec AB [64], [65]. A 3 MW<sub>th</sub> pilot gasifier was set up in Piteå, Sweden in 2005. It was operated in tandem with a methanol and dimethyl ether (DME) synthesis unit between 2011 and 2015. The gasifier was used to test the effect of variations in gasifier and gas quenching operation on the composition and purity of syngas [66]–[68]. These studies concluded that the bulk composition of syngas was principally determined by the water gas shift reaction. It was shown that between 20–25% of the sulfur in BL left the reactor as H<sub>2</sub>S in syngas. An implication of this was that it was possible to recover a fraction of BL sulfur in gaseous form independent of the alkali elements. Once syngas had been cooled and stripped of larger particles, the concentrations of remaining particles were very low and the major non-organic elements present that originated in BL were in the sub-ppm range. Tar concentrations were ~1 ppm.

The process performance of a liquor from a sodium sulfite-based pulp mill was also tested and found to be comparable to that of kraft BL [69]. Nearly complete carbon conversion was reported based on the absence of observable char in the dissolved smelt from the gasifier. However, quantitative estimates of carbon conversion or analyses of the carbon content in the molten smelt returned to the mill were not presented. The absence of relevant measurement and process data meant that complete mass and energy balances for the gasification of kraft BL were not provided, thereby precluding the possibility of carrying out a fully quantitative assessment of gasifier performance and product quality under different operating conditions.

Several studies have investigated the economics of using the BLG concept for the production of a variety of biofuels from BL [62], [65], [70]–[72]. Techno-economic evaluations in recent years have examined the case for blending BL with similar residue-based feedstocks such as pyrolysis oil (PO), crude glycerol and fermentation residues [73]–[75]. These biomass-based feedstocks have a higher organic carbon content than BL and contain few to almost no inorganic components. Blending BL with up to 25 wt.% PO was found to improve energy performance and double the methanol yield [76]. The economic performance of 20–50 wt.% PO blends was found to be better than that of unblended BL for smaller mills in the range of 200–300 kATt/y [74]. The economic case for 50/50 crude glycerol/BL blends was also found to be promising [77].

An investigation into the co-gasification of PO and BL blends found that the char and droplet conversion rates of PO/BL blends with up to 30% PO were similar to those of unblended BL, thereby indicating that the catalytic effect of alkali was still active [78]. The decoupling of biofuel production from BL availability is, however, subject to blending limits, which were found to lie in the 20–25 PO wt.% range for PO/BL blends in lab tests [79]. A higher PO blend fraction led to the precipitation of



lignin, making feeding impractical. The above-mentioned studies on co-gasification were either experimental lab studies or techno-economic evaluations in which gasification performance data was generated by thermodynamic equilibrium calculations (TECs). The conditions in a large pressurized gasifier, such as high flame temperatures, heating rates and alkali release cannot be replicated simultaneously in a lab-scale setup. The practical feasibility of gasifying BL blends in industrially relevant scales was not examined. The effect of blend ratio and gasifier operating parameters on energetic performance and product quality was also not studied.

Gasification experiments in industrially relevant scales are costly and time-consuming. It is generally well established that TECs are useful for mapping and understanding biomass and coal gasification behavior under different process conditions for a range of typical feedstock compositions [80], [81]. In practice, important process parameters such as methane yield, tar formation, char conversion and H<sub>2</sub>S formation deviate significantly from equilibrium, especially for low-temperature processes [82]–[84]. Some of the deviations can be corrected or accounted for by validating TEC results against relevant experimental data. Previously, several thermodynamic equilibrium studies of BLG have been performed [85]–[88]. The two studies that validated TEC results against experimental data focused on equilibrium gas composition only and did not validate the inorganic phase predictions with experimental results. Since, most economic and energetic assessments of BLG are based on TEC results, understanding and improving model behavior is of vital importance. None of the above-mentioned studies have explicitly focused on fully quantifying and understanding the deviation between TEC and experimental results for BLG.

Compared to the gasification-catalytic synthesis route, which has been under development in various guises for a number of decades, the production of biofuels from kraft BL by separation-hydrotreatment is a relatively recent development. Numerous pathways have been put forward but none have reached commercial deployment. There is thus a shortage of detailed technical and techno-economic performance evaluations in the open literature. In Sweden the concepts developed by RenFuel AB [89], SunCarbon AB [90] and SCA AB [91] are currently undergoing technology demonstration.

Anheden et al. [92] assessed the techno-economic viability and environmental impact of drop-in biofuel production from membrane-separated kraft BL lignin and LignoBoost-separated kraft BL lignin by mild hydrothermal liquefaction and base-catalyzed depolymerization, respectively. Their assessment relied on the use of lab-scale data from an early stage of technology development as key process steps in the examined pathways were untested in industrially relevant scales. While the economic case for lignin-based drop-in biofuels appeared similar in robustness to that for forest residue-based biofuels, the former had a larger uncertainty range owing to a significantly lower level of technology maturity that was not quantified or qualitatively discussed explicitly. As a result of intensive R&D work in recent years, the upgrading of membrane-separated kraft lignin to biofuels

has seen a progressive evolution in technology maturity and process configuration with the demonstration of an increasing number of key process steps in pilot-scale [93].

The example of lignin separation-hydrotreatment illustrates how performance evaluations of emerging technologies are often consigned to the use of either non-experimentally validated modelling data or experimental data from an early stage of development, the relevance of which to a commercial plant may be questionable and which may have become obsolete by the time the information enters the public domain.

#### **1.4.2 Techno-Economic Evaluations of Biofuel Pathways**

The economic viability of emerging biofuels is often evaluated by means of techno-economic analysis (TEA) [94]–[96]. In the absence of a standard method, numerous TEA frameworks have been developed and applied to biofuels [97]–[100]. A common approach is that a detailed process model is developed to estimate material and energy flows, which are used in conjunction with estimates of capital expenditure (CAPEX) in a discounted cash flow rate-of-return analysis to determine economic performance [101], [102].

Estimating CAPEX costs of emerging biofuel technologies is a challenging enterprise, especially for FOAK plants [103]. The plurality of approaches available for cost allocation and the lack of a standard framework for risk allocation gives rise to important methodological concerns [104], [105]. Some characteristic examples are the conflation of different types of costs, inaccurate estimation of technology learning rates and allocation of contingency in a manner that does not reflect the expected value of risk [106]–[108].

It has been suggested that the level of granularity at which CAPEX estimates are compiled needs to be aligned with technology maturity to avoid the use of inadequate TEA methods and to facilitate consistent cross-technology comparisons [104]. An argument can therefore be made that evaluating technical, techno-economic or environmental performance of emerging technologies without showing due consideration to technology maturity paints an incomplete picture at best. This is especially pertinent when comparing pathways that are not yet commercially established but have undergone different amounts of pilot testing. Yet estimation of technology maturity using tools such as the Technology Readiness Level (TRL) framework [109] has historically not been accorded a significant role in assessments of emerging biofuel production pathways.

Identification of emerging biofuel production pathways with the lowest environmental and economic costs requires that performance assessments take into consideration other pertinent dimensions besides technical and economic performance. Recent studies in different emerging fields have highlighted the need for systematically evaluating and comparing technology pathways across a range of pertinent performance aspects [110], [111]. The importance of technology maturity has been established earlier, while the necessity of quantifying GHG savings is self-evident given the

climate mitigation and resource efficiency goals discussed in Chapter 1.1. Another important aspect that is of particular relevance to national policymaking and in the study of national energy systems is the biofuel production potential of a pathway.

## 1.5 Thesis Outline

The **first chapter** offers background information to contextualize the interest in biofuels from BL. The concept of biorefining is briefly introduced. The role and prospects of biofuels in the European Union and Sweden are briefly described. A short overview of chemical pulping and a perspective on how and why biofuels and pulp and paper mills can come together is provided. Various options for the production of biofuels from kraft BL are introduced and a survey of the academic literature on their study and evaluation is included.

The **second chapter** enumerates the research questions that this thesis attempts to answer.

The **third chapter** provides schematic overviews and process descriptions of the examined biofuel pathways. It also outlines the pulp mills and the crude oil refinery with which different stages of biofuel production are co-located and integrated.

The **fourth chapter** details the different methods used in the investigation of the research questions. These include pilot-scale gasification experiments (Chapter 4.1), TECs (Chapter 4.2), TEAs (Chapter 4.3), TRL assessments (Chapter 4.4) and simplified GHG footprint estimation (Chapter 4.4).

The **fifth chapter** presents research results. The first research question, which concerns the gasification performance of BL and PO blends in pilot-scale experiments is addressed in Chapter 5.1. The second research question, which concerns thermodynamic equilibrium calculations of BLG is addressed in Chapter 5.2. The third and fifth research questions, which concern the economics of biofuels from BL are addressed in Chapter 5.3. The fourth research question, which concerns the evaluation of other relevant aspects important for commercial deployment is addressed in Chapter 5.4.

The **sixth chapter** summarizes the findings of the research that was carried out to answer the questions formulated in Chapter 2. A number of general conclusions and reflections are also presented. The thesis closes with a number of suggestions for further research.

## 2 Research Questions

*This chapter enumerates the research questions that this thesis attempts to answer.*

The backdrop is this: Efforts to reduce GHG emissions in transport are taking on increased importance. Countries with extensive forest industries see forest-based biofuels as a strategically vital resource for emission mitigation in the near-to-medium term. One of the principle users of forest biomass is the pulp and paper industry, which generates a by-product known as BL that is rich in lignin.

The main aim of this thesis is to evaluate the technical and economic viability of industrially relevant pathways that can be used to produce biofuels from kraft BL. Industrially relevant pathways are pathways that are seen as candidates for mass deployment in the short-to-medium term from the perspective of an observer in the year 2018.

The evaluation of technical viability is focused on the study of kraft BL and fast PO co-gasification as a part of the continued development of the gasification step in the gasification-catalytic synthesis route. The co-gasification of PO/BL blends in pilot-scale experiments is carried out with the aim of answering the following research question:

**Question 1:** *How is gasification performance influenced by blending black liquor with up to 20% pyrolysis oil by weight? (Papers I & II)*

To answer the above question, data generated in the pilot-scale experiments is used to compile comprehensive mass and energy balances for unblended black liquor and a number of PO/BL blends. The mass and energy balances are used to quantify key performance indicators, such as syngas quality, cold gas efficiency, green liquor (GL) quality and carbon conversion efficiency. Further information on performance indicators can be found in Chapter 4.1.5.

Pilot-scale experiments are time-consuming and expensive. The range of feasible operating conditions is limited by practical considerations. Thermodynamic equilibrium calculations (TEC) can offer a quicker and more cost-effective means of estimating product yields and gasification performance. To investigate the utility of TEC predictions, the following question is posed:

**Question 2:** *Can thermodynamic equilibrium calculations of entrained-flow black liquor gasification predict product compositions and gasification performance to a high degree of accuracy? (Paper III)*

An answer is sought by validating TEC predictions against experiments results, including some from pilot-scale experiments carried out to investigate Question 1, for a range of operating conditions. To improve process understanding, the sensitivity of TECs to variations in important process inputs is also examined.

The economic case for biofuels from BL bears examination and an important question is as follows:

**Question 3:** *What does an evaluation based on best available experimental data reveal about the economic viability of producing biofuels from black liquor?* (Papers IV, V and VI)

The economic performance of a number of pathways from industrially relevant technology tracks is techno-economically evaluated using performance indicators such as profitability and production costs. As a part of the techno-economic evaluation, the energy performance is also examined using, where appropriate, TECs (see Question 2) for modelling BLG gasification. Further details on the techno-economic evaluation methodology can be found in Chapter 4.3. An assessment of the profitability of BL pathways relative to that of other industrially relevant forest-based pathways is provided to see how the different alternatives compare in economic performance.

The economic viability of biofuel production technologies is also directly and indirectly influenced by factors such as technology maturity, GHG performance and biofuel production potential. An examination of these aspects can serve as an important input to overall performance assessments, which is why the following question is considered:

**Question 4:** *How do the most industrially relevant pathways for the production of biofuels from black liquor compare with each other in terms of technology maturity, greenhouse gas emissions and biofuel production potential?* (Papers IV, V and VI)

Energy balance models compiled for techno-economic evaluations (see Question 3) are used in conjunction with the TRL methodology, RED guidelines for GHG footprint estimations and literature estimates of feedstock potentials, respectively, to evaluate technology maturity, GHG emissions and biofuel production potentials.

Kraft BL is typically combusted in a RB, which is a bottleneck to capacity expansion at some pulp and paper mills. Redirecting some of the BL to a gasifier (or a lignin separation unit) can generate capacity in the RB, which can be used to increase pulp production, provided other bottlenecks are absent or mitigated against. For pulp mills, the increased pulping capacity can, in conjunction with the sale of produced biofuels, translate into significant additional revenue. The biofuel production potential, and possibly the economics, of small-scale gasification-based “debottlenecking” units can be improved through the use of secondary feedstocks such as PO, as per the route investigated in relation to Question 1, and/or electrolysis hydrogen. An evaluation of the economic performance of small debottlenecking BLG units integrated with different types of mills and a determination of whether said performance can be improved through feedstock expansion is the topic of the two-part fifth and final question.

**Question 5:** *How do gasification-based pathways perform economically when used to produce biofuels from part streams of BL and how is economic performance influenced by the use of pyrolysis oil and electrolyzer hydrogen as secondary feedstocks?* (Paper VI)

An answer is found by carrying out techno-economic modelling to estimate the cost of producing biofuels for selected gasification-based pathways in relation to that of lignin separation-based alternatives. Based on findings from Paper V, the impact of mill energy requirement on integrated energy balance and biofuel costs is also investigated.



### 3 Biofuel Production Systems

*This chapter provides schematic overviews and process descriptions of the examined biofuel pathways. Overviews of the pulp mills and the crude oil refinery with which different stages of biofuel production are co-located and integrated are also given.*

#### 3.1 Biofuel Pathways

The BL-based biofuel pathways evaluated in this thesis are listed in Table 1. Two belong to the separation-hydrotreatment route and five to the gasification-catalytic synthesis route. The lignin separation-hydrotreatment route is used to produce drop-in fuels from BL lignin. The gasification-catalytic synthesis route allows for a degree of product flexibility as it can be used to manufacture both high blend and drop-in fuels from kraft BL.

**Table 1. Overview of studied biofuel pathways.**

Pathway	Paper	Route	Feedstock(s)	Product(s)	Integration [Mill/Refinery]
BLG-MEOH	I, III, IV, V	Gasification-Catalytic Synthesis	Black Liquor	Methanol	✓/✗
CO-BLG-MEOH	II	Gasification-Catalytic Synthesis	Pyrolysis Oil & Black Liquor	Methanol	✓/✗
BLG-PTRL	VI	Gasification-Catalytic Synthesis	Black Liquor	Petrol & LPG	✓/✓
EL-BLG-PTRL	VI	Gasification-Catalytic Synthesis	Electricity & Black Liquor	Petrol & LPG	✓/✓
CO-BLG-PTR	VI	Gasification-Catalytic Synthesis	Pyrolysis Oil & Black Liquor	Petrol & LPG	✓/✓
MSL-HDO	IV, V, VI	Lignin Separation-Hydrotreatment	Black Liquor (Lignin)	Petrol & Diesel	✓/✓
MSL-HDO-EL	VI	Lignin Separation-Hydrotreatment	Black Liquor (Lignin)	Petrol & Diesel	✓/✓

In BLG-MeOH and CO-BLG-MeOH, biofuel production is co-located and integrated with a pulp mill and the final biofuel product is AA grade methanol. In all other pathways, BL is first upgraded to a transportable intermediate at the mill, namely, stabilized methanol in the gasification-catalytic synthesis route and a stabilized lignin/vacuum gas oil (VGO) mix in the lignin separation-hydrotreatment route. The intermediate is then shipped to a crude oil refinery for upgrading to transport fuels such as petrol, diesel and liquefied petroleum gas (LPG). An overview of each pathway is provided below together with information on evaluated performance aspects and methods used for carrying out the said evaluations.

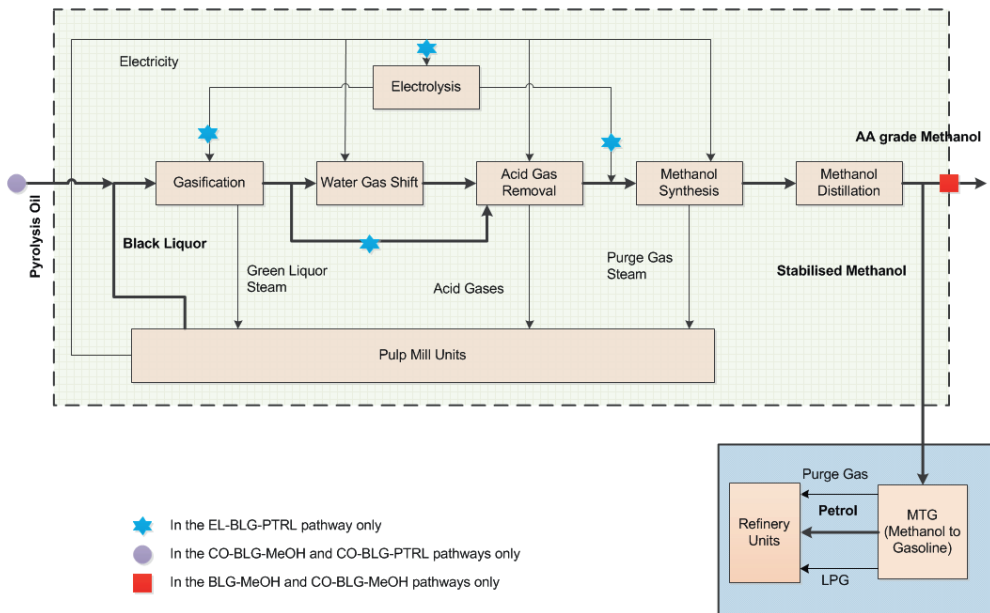
##### 3.1.1 The Gasification-Catalytic Synthesis Route

A simplified process schematic of the gasification-catalytic synthesis route showing the process configurations of constituent pathways is provided in Figure 2.



## BLG-MeOH

Syngas from entrained-flow gasification of kraft BL is upgraded to AA grade methanol. The gasification performance of kraft BL is experimentally studied in Papers I and II. Results from Paper I are included in the experimental dataset used to assess whether TECs be used for predicting BLG performance as discussed in Paper III. A detailed energy and mass balance model based on best available data was used to evaluate the entire process chain in the multi-aspect performance evaluation study presented in Papers IV and V.



**Figure 2. Simplified process schematic for the gasification-catalytic synthesis route. There is no water gas shift in the EL-BLG-PTRL pathway, syngas is sent for acid gas removal directly.**

BL is gasified in a pressurized refractory-lined reactor using oxygen as both the oxidizing and the atomizing agent. The alkali metals in BL catalyze char gasification reactions and help break down tar and soot, which results in a clean syngas and nearly complete carbon conversion at relatively low temperatures  $\sim 1000$  °C. The major components in syngas after drying are CO, H<sub>2</sub> and CO<sub>2</sub>. Minor components are H<sub>2</sub>S and CH<sub>4</sub>. Some higher hydrocarbon species, principally C<sub>6</sub>H<sub>6</sub>, are present in ppm<sub>v</sub> concentrations. Alkaline cooking chemicals in BL form a molten slag, which is dissolved in water and returned to the mill for reuse. After leaving the reactor, syngas is cooled to  $\sim 30$ - $40$  °C in two stages: first by rapid quenching and afterwards in a counter-current condenser that acts as a particle scrubber and permits heat recovery. To meet the stoichiometric requirement for methanol synthesis, syngas composition is adjusted in a water-gas shift reactor after which CO<sub>2</sub> and H<sub>2</sub>S are

separated in a Rectisol® acid-gas removal unit. The conditioned syngas is catalytically upgraded to crude methanol, which is distilled to produce AA grade methanol. Heat from syngas conditioning and methanol synthesis is used internally and excess is exported to the pulp mill.

### **CO-BLG-MeOH**

Syngas from entrained-flow gasification of kraft BL and fast PO blends is upgraded to AA grade methanol. Gasification performance of PO/BL blends with up to 20 wt.% PO is experimentally studied in Paper II. Note that CO-BLG-MeOH is not evaluated techno-economically in this work. Since CO-BLG-MeOH has the same process configuration as BLG-MeOH with the exception of an additional unit used for pre-mixing PO/BL blends, it is not described here in greater detail.

### **BLG-PTRL**

Syngas from entrained-flow gasification of kraft BL is upgraded first to methanol and then to petrol blendstock. A detailed energy balance model based on best available data is used to evaluate the energy performance, economic viability and GHG performance of BLG-PTRL in Paper VI. The process configuration up to and including the synthesis of crude methanol is the same as in BLG-MeOH with the following exceptions. Oxygen for the gasifier is purchased over the fence rather than being produced on site in a cryogenic air separation unit. Acid gases are removed by amine scrubbing, a chemical separation process that washes out CO<sub>2</sub> and H<sub>2</sub>S simultaneously. Amine scrubbing has a lower capital cost than Rectisol®-based acid gas removal, albeit at the expense of significantly greater steam consumption and a loss of sulfur selectivity. Amine scrubbers cannot reliably reduce the concentration of H<sub>2</sub>S in syngas to below 10 ppm<sub>v</sub>. A zinc bed is therefore used to reduce the concentration of sulfur to below 0.1 ppm<sub>v</sub> and thereby avoid the deactivation of synthesis catalysts. Compared with AA grade methanol, stabilized methanol requires the use of fewer distillation columns. The synthesis of petrol from methanol through the methanol-to-gasoline (MTG) process is carried out at a crude oil refinery to take advantage of existing infrastructure [112], [113]. DME is produced in an intermediate step. Gaseous by-products from the synthesis loop are combusted for energy recovery.

### **EL-BLG-PTRL**

BL from the pulp mill is gasified to produce syngas, which is mixed with hydrogen from polymer electrolyte membrane (PEM) electrolysis of water before being upgraded first to syngas and later to petrol. The energy performance, economic viability and GHG performance of EL-BLG-PTRL are evaluated in Paper VI. EL-BLG-PTRL can be viewed as a variant on BLG-PTRL with improved utilization of the organic fraction in the feedstock, thereby leading to higher product yields from the same amount of BL. The process configuration, which is shown on Figure 2 differs from that of other gasification-based pathways in some notable aspects. There is no water gas shift unit. The stoichiometric requirement for methanol synthesis is met by adding H<sub>2</sub> from the electrolysis of water in a PEM electrolyzer to syngas after the removal of acid gases by amine scrubbing.

## CO-BLG-PTRL

Syngas produced from entrained-flow gasification of kraft BL and fast PO blends is upgraded firstly to methanol and later to petrol. The energy performance, economic viability and GHG performance of CO-BLG-PTRL is studied in Paper VI together with that of the other gasification-based drop-in pathways. CO-BLG-PTRL has the same process configuration as BLG-PTRL and the only difference between the two is that the former uses PO/BL blends as feedstocks, while the latter uses unblended BL.

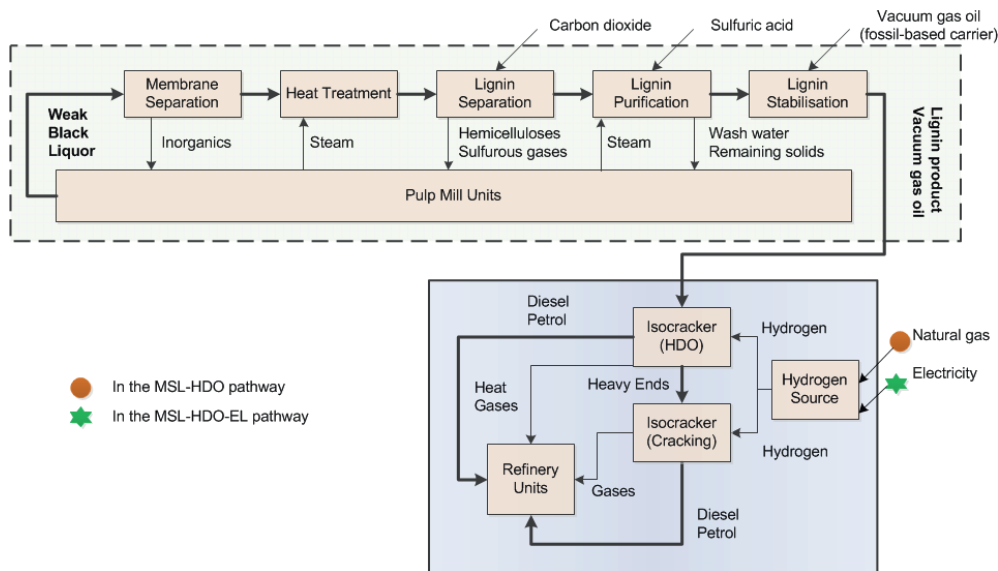
### 3.1.2 The Separation-Hydrotreatment Route

A simplified process schematic of the separation-hydrotreatment route showing the process configurations of constituent pathways is provided in Figure 3.

#### MSL-HDO

Lignin is separated from kraft BL, purified, stabilized and sent to an oil refinery for hydrotreatment and upgrading to petrol and diesel blendstock. MSL-HDO is based on lignin separation and purification technology from Sun Carbon AB [114]. MSL-HDO is studied in Papers IV and V, where it was techno-economically evaluated using a process spreadsheet energy balance model based on best available technical data in the literature. Following the release of new experimental data, the process configuration was updated and an improved model was used in the techno-economic evaluation presented in Paper VI. The description below is of the updated configuration.

The aim of the lignin separation stage is to obtain a stable lignin product free of alkaline impurities that can be transported to an oil refinery for co-processing with crude oil derivatives. A stream of weak BL is extracted at an early stage in the evaporation cycle and sent to a membrane separation unit. The lignin and hemicellulose fractions in the feed are held back in the retentate stream, while the alkali compounds in the alkali-rich permeate stream are returned to the evaporation unit. The heat treatment of the permeate with steam initiates an alkali-catalyzed breakdown of hemicelluloses. The residual products of the reaction are also returned to the evaporation unit. The depolymerized lignin fragments are acidulated with CO<sub>2</sub>, which reduces the pH and leads to the formation of a liquid lignin phase by protonation. Impurities still present at this stage are leached out by washing the mixture with sulfuric acid. An organic solvent is used to generate a stable 50/50 mixture of lignin and a fossil carrier oil, namely, vacuum gas oil (VGO) with negligible alkali content that can be transported and processed at the crude oil refinery.



**Figure 3. Simplified process schematic for the separation-hydrotreatment route. All process steps except the production of hydrogen for hydrotreatment are shared between MSL-HDO and MSL-HDO-EL.**

At the refinery, the lignin/VGO mixture is further diluted with VGO and fed to a two-step isocracker that can process feeds with up to 5 wt.% oxygen. Chemically bound oxygen and sulfur are removed by treating the feed with hydrogen at elevated temperature and pressure in the presence of a catalyst. Some saturation of aromatics also takes place. The product mix from the first step is dominated by diesel components and contains heavy hydrocarbons, which are broken down into smaller hydrocarbons in the second step. The hydrogen for the hydrotreatment of lignin is produced by steam reforming of natural gas.

### MSL-HDO-EL

The economic viability of MSL-HDO-EL is techno-economically evaluated in Paper VI. MSL-HDO-EL has the same process configuration as MSL-HDO and the only difference between the two is that the former uses natural gas-based hydrogen for hydrotreatment, while the latter uses hydrogen from PEM electrolysis of water.

## 3.2 Pulp Mills

The synergies and trade-offs between different mill configurations and biofuel pathways are assessed by evaluating the integration of biofuel production with three mills that have different production capacities and contrasting energy profiles. In Papers IV and V, all but one of the pathways are co-located and integrated with a simulation model of a state-of-the-art market pulp



at 120 bar (a). Two additional boilers are also present that are typically not in use during normal operation. The lime kiln is fired with sawdust, pellets and bio oil. While some electricity is generated by two back pressure turbines, SKKP is a net importer of electricity from the grid.

The Södra Cell Mörrum (Södra) mill is a market pulp mill with a combined paper and textile pulping capacity of 1288 tons/day. The process demand for steam is principally supplied by the RB, which produces high pressure steam at 58 bar(a). The limekiln is fired with tall oil residue. The mill is equipped with an auxiliary biomass boiler for backup. Although there is an excess of steam relative to process demand, the surplus cannot be converted into electricity due to a lack of capacity in the existing turbines and the absence of a condensing turbine [115].

### **3.3 Crude Oil Refinery**

Biofuel production is co-located and integrated with a refinery modeled on Preem Oil Refinery, Lysekil. The Lysekil refinery has a crude oil refining capacity of 11.4 Mt/yr with a gross energy demand in excess of 400 MW<sub>th</sub>, which is supplied by internally produced energy gases and externally purchased natural gas. The refinery is home to a vacuum distillation unit with a capacity of 1000 cubic meter per day. The VGO from the vacuum distillation unit is processed in a two-step iso-cracker, which is assumed to have been rebuilt to handle biogenic feedstock such as lignin in blends with VGO. The hydrogen supplied for process use in the refinery is principally produced by steam reforming of natural gas. The product range at the Lysekil refinery includes petrol, diesel, LPG and various grades of fuel oil.



## 4 Methods

*This chapter describes the methods used to investigate the research questions. The first sub-chapter gives an overview of pilot-scale gasification experiments and provides information on experimental conditions, feedstock composition, media analysis and gasification performance indicators. The second sub-chapter describes how the thermodynamic equilibrium calculations of BLG were performed and gives relevant background information. The third sub-chapter reviews the economic evaluation approach as well as the energy and economic performance indicators used in this work. A description of the process models for the examined pathways is also given. The final sub-chapter shortly covers the methodology used to evaluate technology maturity, biofuel production potentials and GHG emission performance.*

### 4.1 Pilot-Scale Gasification Experiments

(Paper I and II)

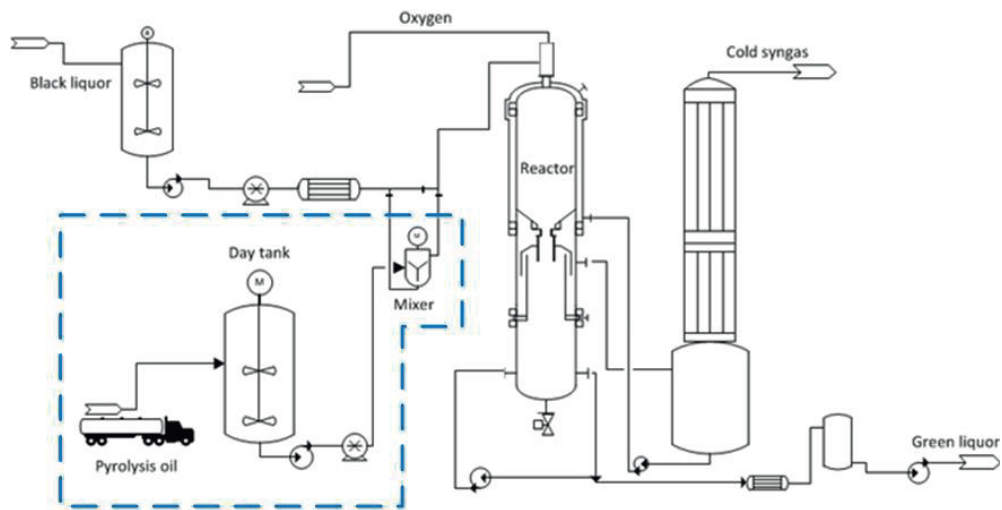
The co-gasification of kraft BL and fast PO is studied in pilot experiments performed at the LTU Green Fuels plant in Piteå, Sweden. In the lead-up to co-gasification experiments, a pre-study was carried out to quantitatively evaluate the gasification performance of unblended kraft BL under different reactor conditions. The results, which are detailed in Paper I provided a frame of reference for the design and evaluation of co-gasification experiments. PO/BL blends with up to 20 wt.% PO were successfully gasified in an experiment designed to evaluate the impact of blend ratio and reactor temperature on co-gasification performance. The results are presented in Paper II.

#### 4.1.1 Experimental Setup

The gasification unit at the LTU Green Fuels plant was built in 2005 by Chemrec AB to demonstrate and study the technical viability of BLG technology. Since 2011, it has been connected to a biofuel synthesis facility that can produce methanol and DME. A simplified schematic of the gasification unit is given in Figure 5. BL and PO are pre-mixed before gasification to avoid the formation of pH and temperature gradients. The pressurized feed from the mixer enters the refractory-lined reactor vessel at the top through a co-annular nozzle. Inside the reactor, the feed is atomized and oxidized by a stream of oxygen. The ensuing reactions produce syngas rich in CO and H<sub>2</sub> and smelt made up of carbonate and sulfide salts of alkali metals.

After exiting the reactor both smelt and syngas are cooled by water sprays in a narrower section of the vessel known as the quench tube. The orientation of the spray nozzles influences the cooling rate, which in turn affects syngas composition as a result of the temperature dependence of the water-gas shift and hydrolysis reactions [116]. The cooled smelt dissolves in a pool of wash water at the bottom of the gasifier vessel, which is known as the green liquor (GL) dissolver and a water-sealed pump is used to keep the GL in continuous circulation to avoid sedimentation.





**Figure 5.** A simplified schematic of the experimental setup used in gasification and co-gasification experiments. Major streams and components are marked. The process area denoted by the dashed rectangle was used in co-gasification experiments (Paper II) only.

Syngas is further cooled by an additional set of nozzles on its way out of the quench tube. It is bubbled through a water lock and leaves the reactor for a vertically mounted gas cooler where it is indirectly cooled down to 30-40°C through heat exchange with water in two shell-and-tube heat exchangers arranged in series. The drop in temperature causes water vapor in the gas to condense and fall down the exchanger tubes into a condensate reservoir, thereby stripping the gas of entrained particles in the process. The condensate reservoir is used to feed the aforementioned sprays as well as liquid films used to cool various gasifier vessel surfaces (see Process Description in Paper I for more details on the sprays and films). Plant control is configured to ensure that the level of the gas condensate in the pool never falls below a minimum threshold. Excess flow is discharged to the GL dissolver from where it eventually exits the system as GL bound for the pulp mill.

#### 4.1.2 Experimental Conditions

Experimental runs were designed to assess gasifier performance over as wide an operating range as possible while satisfying GL quality requirements and staying within operational constraints on parameters such as feed atomization. An overview of operating condition is provided in Table 2. The methane content in syngas was monitored in real time with the help of a nondispersive infrared sensor and used as a marker of gasifier temperature. It was found to be a more consistently reliable indicator of reactor temperature than thermocouple readings, which were susceptible to conductive interference from the wall and radiation from the very hot flame in the upper part of the reactor. A strong inverse correlation between reactor temperature and the methane concentration in syngas

has previously been experimentally established for entrained-flow gasification of solid biomass [117] and sulfite thick liquor (STL) [69].

**Table 2. Process settings for pilot-scale experiments.**

Operating Point (OP)	Black Liquor Input	Pyrolysis Oil Input	$\lambda$ <sup>j</sup>	Pressure	Feedstock Energy Input <sup>k</sup>	Feedstock Alkali-to-Carbon (Na+K)/C
	[kg/hr]	[kg/hr]	[-]	[bar(g)]	[MW <sub>th</sub> ]	[mol/mol]
<i>In Paper I</i>						
BL only "Typ" <sup>a,b</sup>	1250	N/A	0.491	28.8	3.05	0.413
BL only "Hot" <sup>c</sup>	1250	N/A	0.505	28.7	3.07	0.410
BL only "RT" <sup>d</sup>	1060	N/A	0.486	27.4	2.59	0.412
BL only "LP" <sup>e</sup>	1060	N/A	0.493	24.1	2.59	0.412
<i>In Paper II</i>						
BL only "Std." <sup>f,g</sup>	1103	N/A	0.454	27.6	2.81	0.369
10/90 PO/BL	887	100	0.453	27.5	2.74	0.308
15/85 PO/BL "Std." <sup>f</sup>	812	145	0.442	27.3	2.76	0.282
20/80 PO/BL	733	185	0.448	27.3	2.73	0.258
BL only "Cold" <sup>h</sup>	1100	N/A	0.437	27.1	2.77	0.373
15/85 PO/BL "Cold" <sup>h</sup>	805	145	0.437	27.2	2.71	0.282
BL only "Hot" <sup>i</sup>	1104	N/A	0.466	27.7	2.81	0.368
15/85 PO/BL "Hot" <sup>i</sup>	806	145	0.469	27.3	2.73	0.283

<sup>a</sup> "Typical" OP for the pilot gasifier, denoted by a feedstock throughput of ~3.1 MW<sub>th</sub> and a syngas methane content of ~1 mol%.

<sup>b</sup> Average of two independent runs at the same nominal OP.

<sup>c</sup> "Hot" is characterized by a syngas methane content of ~0.5 mol%, thereby exemplifying an OP with elevated oxygen consumption.

<sup>d</sup> "RT" denotes an OP with a longer residence time, achieved by reducing feedstock throughput while keeping gasifier pressure constant.

<sup>e</sup> "LP" represents gasifier operation at reduced pressure but with the same nominal residence time as in "typical" operation.

<sup>f</sup> "Std." is characterized by a syngas methane content of ~1.2 mol% in syngas.

<sup>g</sup> Average of three separate runs at the same nominal OP.

<sup>h</sup> "Cold" is characterized by a syngas methane content of ~2.1 mol%.

<sup>i</sup> "Hot" is characterized by a syngas methane content of ~0.5 mol%.

<sup>j</sup> Ratio of gasifier oxygen consumption to the stoichiometric requirement for a given mixture.

<sup>k</sup> On higher heating value basis.

The effect of blend ratio was examined by gasifying blends with PO/BL ratios of 10/90, 15/85 and 20/80 on a mass basis while keeping the total thermal load unchanged. Since the heating value of PO is higher than that of BL, the total feedstock flow decreased with an increase in PO blend fraction. The effect of reactor temperature on the gasification of unblended BL and a 15/85 PO/BL blend was studied by varying the methane content between 0.5 mol% and 1.9 mol%. Note that PO/BL blends are presented in terms of their molar alkali-to-carbon ratios. A decrease in the alkali-to-carbon ratio corresponds to an increase in the fraction of PO in the PO/BL blends.

Reactor temperature has been shown to be a nearly linear function of the  $\lambda$  value in entrained-flow gasification at steady-state conditions [118]. As can be seen from a comparison of the relative positions of unblended kraft BL and a 10/90 PO/BL blend in Figure 2 of Paper II, two different feedstocks that are likely to yield syngas with significantly different compositions can still have very

similar  $\lambda$  values. By definition,  $\lambda$  does not explicitly account for the oxygen found in the feedstock, which in many instances is available to gasification reactions. A unique description of the total oxygen available for gasification is provided by the relative oxygen content (ROC), which is defined in eq. 1 as follows [119]:

$$ROC = \frac{O_{2\_additional} + O_{2\_feedstock}}{O_{2\_stoich} + O_{2\_feedstock}} \text{ (Eq. 1)}$$

$O_{2\_additional}$  is the quantity of oxygen gas added as an oxidant,  $O_{2\_feedstock}$  is the quantity of oxygen found in the feedstock and  $O_{2\_stoich}$  is the quantity of oxygen gas required for stoichiometric combustion. As shown in Figure 2 of Paper II, each feedstock has a unique ROC value, which is proportional to the  $\lambda$  value, and thus to reactor temperature, for that feedstock. ROC is used to present results from investigations of temperature variations as it gives a feedstock independent description of the total oxygen available for gasification reactions.

#### 4.1.3 Feedstock Composition

The elemental compositions of BL and PO are presented in Table 3. As a pulping by-product, kraft BL has a composition that is atypical of most lignocellulosic residues. Approximately two-thirds of the solids content is made up of lignin fragments and polysaccharide degradation products. The remainder consists of inorganic salts of alkali metals with sodium as the most abundant element. Fast PO, in comparison with BL, contains significantly more carbon, marginally more oxygen, and virtually no ash, which means that it has a significantly greater heating value.

#### 4.1.4 Process Data Measurements, Media Sampling & Analysis Procedures

The mass flows of BL, PO, GL and syngas were measured with Coriolis flow meters. All other flows were measured with orifice flow meters. A number of calibrations were performed to improve the accuracy of key flow measurements, especially those of syngas and GL. More details are provided in the section titled “Experimental Conditions” in Paper I and in section “A1” of the Supplementary Information for Paper II. Reactor temperature was monitored with the aid of seven thermocouples arranged in three vertical rows along the reactor walls.

The moisture content of the BL feed from the mill was monitored using an online refractrometer, which provided calibration data for lab measurements based on collected samples. Fluctuations in the moisture content of BL and the chemical composition of BL DS meant that the carbon content of the gasifier feed saw variations of up to 2 wt.% over the course of multi-day experiments. Such variations were partially corrected for by averaging measurements from the beginning and the end of each experiment.

**Table 3. Chemical composition of kraft black liquor and fast pyrolysis oil based on averaged measurements from samples taken in pilot-scale experiments.**

	Unit	Kraft Black Liquor [Paper I]	Kraft Black Liquor [Paper II]	Fast Pyrolysis Oil [Paper II]	Lab	Measurement technique
C	wt.% DS	27.50 <sup>a</sup>	29.64 <sup>d</sup>	53.64	SP <sup>f</sup> /VTT <sup>g</sup>	CHN analyzer <sup>k</sup>
H	wt.% DS	3.75 <sup>a</sup>	3.69 <sup>d</sup>	6.35	SP <sup>f</sup> /VTT <sup>g</sup>	CHN analyzer
N	wt.% DS	0.07 <sup>a</sup>	0.14 <sup>d</sup>	0.14	SP <sup>f</sup> /VTT <sup>g</sup>	CHN analyzer
Cl	wt.% DS	0.16 <sup>a</sup>	0.14 <sup>d</sup>	-	SP <sup>f</sup>	Ion chromatograph
Na	wt.% DS	19.85 <sup>b</sup>	18.99 <sup>e</sup>	-	ALS <sup>h</sup>	ICP- AES/SFMS
K	wt.% DS	3.12 <sup>b</sup>	3.55 <sup>e</sup>	-	ALS <sup>h</sup>	ICP- AES/SFMS
S	wt.% DS	6.20 <sup>c</sup>	6.15 <sup>e</sup>	-	ALS <sup>h</sup>	ICP- AES/SFMS
O	wt.% DS	39.35	37.70	39.87	-	By difference
Moisture content	wt.%	27.54	26.80	29.9	SP <sup>f</sup> /LTU	Drying and
	Feedstock				GF <sup>i</sup> /VTT <sup>g</sup>	weighing/Karl Fischer titration <sup>m</sup>
HHV <sup>o</sup>	MJ/kg DS	12.13	11.75 <sup>d</sup>	16.84	SP <sup>f</sup> /LTU ENE <sup>j</sup>	Bomb calorimetry
TAN <sup>p</sup>	mg KOH/g	-	-	64.4	VTT <sup>g</sup>	Potentiometric titration <sup>n</sup>

<sup>a</sup> Average of measurements from two different operating points (OPs).

<sup>b</sup> Average of measurements from four different OPs.

<sup>c</sup> Average of measurements from five different OPs.

<sup>d</sup> Average of measurements from two different OPs.

<sup>e</sup> Average of measurements from ten OPs.

<sup>f</sup> RISE Research Institutes of Sweden (Borås).

<sup>g</sup> Fast pyrolysis oil samples were analysed by VTT Technical Research Centre of Finland (Espoo).

<sup>h</sup> ALS Scandinavia (Luleå).

<sup>i</sup> LTU Green Fuels Plant (Internal, calibrated with an online refractrometer).

<sup>j</sup> LTU ENE Lab (Internal).

<sup>k</sup> ASTM D 5291.

<sup>l</sup> SS EN ISO 11885 (modified).

<sup>m</sup> For determining the moisture content of fast pyrolysis oil as per ASTM E 203.

<sup>n</sup> ASTM D 664.

<sup>o</sup> Higher heating value

<sup>p</sup> Total acid number

It is important that media samples and process data used for performance analysis are collected under steady-state conditions. The residence time of syngas in the gasification reactor is in the order of a few seconds, while the hydraulic residence time of GL in the GL dissolver is estimated to be around 1.9 hours [69]. Each operating point (OP) was maintained for a minimum of 6 hours and media samples were generally taken immediately before the switchover. More information on sampled streams and analytical procedures is provided in Table 4.

#### 4.1.5 Gasification Performance Indicators

BLG produces two product streams: (a) syngas, which is upgraded to biofuels, (b) GL, which is returned to the pulp mill for the recovery of cooking chemicals. The quality of both product streams needs to be considered when evaluating the effect of changes in gasifier operation. Cold gas efficiency (CGE) and carbon conversion efficiency are two measures of gasification performance

linked to syngas quality and GL quality, respectively, as discussed below. Mass and energy balance closures are important for establishing confidence in the accuracy of the data underpinning performance assessments.

**Table 4. Analytical methods used to determine the contents of process streams other than the feed.**

Media	Component	Lab	Measurement Method	Standard
<b>green liquor</b>	Na, K, S	ALS <sup>d</sup>	ICP-AES	SS EN ISO 11885 (modified)
	Filtrate TIC <sup>a</sup>		TOC analyzer <sup>h</sup>	ISO 8245
	Filtrate TOC <sup>b</sup>			ISO 8245
	Suspended solids “sludge” content	MoRe <sup>e</sup>	Filtration	T 692 om -93
	CO <sub>3</sub> <sup>2-</sup> , HCO <sub>3</sub> <sup>-</sup> , HS <sup>-</sup>		acid titration	SCAN-N 32 SCAN-N 31
<b>condensate</b>	HCOO <sup>-c</sup>	Innventia <sup>f</sup>	IC-CD <sup>i</sup>	N/A
	Na, K, S	ALS <sup>d</sup>	ICP-AES	SS EN ISO 11885 (modified)
	TIC	MoRe <sup>e</sup>	TOC analyzer <sup>h</sup>	ISO 8245
<b>syngas</b>	TOC			ISO 8245
	All components	SP ETC <sup>g</sup>	Gas chromatography <sup>j</sup>	N/A

<sup>a</sup> Total inorganic carbon.

<sup>b</sup> Total organic carbon.

<sup>c</sup> Formate Ion.

<sup>d</sup> ALS Scandinavia, Luleå.

<sup>e</sup> MoRe Research, Örnsköldsvik.

<sup>f</sup> Innventia AB, Stockholm.

<sup>g</sup> SP Energy Technology Center, Piteå (presently a part of RISE Swedish Institutes of Technology).

<sup>h</sup> Shimadzu, Model TOC-5050.

<sup>i</sup> Ion chromatography with conductivity detection.

<sup>j</sup> Varian CP-3800.

## Syngas Quality and Gasifier Cold Gas Efficiency

The quality of syngas is evaluated in terms of its chemical composition, which is determined by chromatographic analysis of collected gas samples. The major species in syngas from BLG are CO, H<sub>2</sub> and CO<sub>2</sub>. The most notable minor species are CH<sub>4</sub>, H<sub>2</sub>S and N<sub>2</sub>. COS and C<sub>6</sub>H<sub>6</sub> are found in ppm<sub>v</sub> concentrations. Trace amounts of other higher hydrocarbon species are also present. In general, the quality of syngas intended for methanol synthesis improves as its CO and H<sub>2</sub> content increases, provided that the content of tars and other impurities is kept low. A characteristic of BLG is that the fraction of sulfur that ends up in syngas as H<sub>2</sub>S and COS can be recovered and either returned to the RB or upgraded, depending on mill requirements. The ratio of sulfur in syngas to that in gasifier feed is referred to as the sulfur split.

CGE is a commonly used measure of the efficiency of energy conversion, which has been defined as the “ratio of the chemical energy in the product gas to that in the feedstock”[120]. CGE can be calculated in different ways, depending on the choice of the species present in syngas, typically determined by its intended end use. CGE<sub>Power</sub> is calculated as the ratio of the chemical energy in all combustible syngas constituents to that in the feedstock. CGE<sub>Fuel</sub> is calculated as the ratio of the chemical energy in CO and H<sub>2</sub> to that in the feedstock. CGE<sub>Fuel+S-free</sub> is calculated as the ratio of the

chemical energy in CO and H<sub>2</sub> to that in the feedstock minus the enthalpy of oxidation of its sulfur fraction. Since the BLG process requires that sulfur is returned to the pulp mill as reduced sulfides of sodium and potassium, it is assumed that the energy associated with sulfur oxidation is not available for gasification reactions.  $CGE_{\text{Fuel}+\text{S-free}}$  can be considered the most representative measure for evaluating the energy efficiency of biofuel production from BL blends, although  $CGE_{\text{Fuel}}$  is also used in this work.

### Green Liquor Quality and Carbon Conversion Efficiency

Several indicators are used to evaluate different aspects of GL quality. Sludge content is used to quantify the amount of organic and inorganic solids in GL. Sulfur reduction efficiency is the fraction of sulfur in GL that is present in the form of HS<sup>-</sup> ions, which signifies the useful form of sulfur in the kraft process. The total inorganic carbon (TIC) content represents the carbon present in inorganic form, which is returned to the mill. The total organic carbon (TOC) content is a measure of the amount of carbon present as unconverted, partially converted or dissolved organic fragments. TOC is used to estimate the carbon conversion efficiency of the gasifier as described below.

A common definition of carbon conversion efficiency found in the literature on thermochemical conversion of biomass is the following: the ratio of carbon available in gaseous and liquid products to the total amount of carbon in biomass [121]. The above definition cannot be applied to BLG in a straightforward manner as the recovery of the inorganic carbon in GL solids is an integral part of the process. Furthermore, the gasification of both unblended BL and PO/BL blends yields syngas that is virtually free of tars [67]. The cooling of syngas in the BLG process is designed to ensure that unconverted or partially converted organic fragments are returned to the GL dissolver. Thus, an alternative definition of carbon conversion efficiency for the BLG process that is easier to measure experimentally is proposed as follows in eq. 2:

$$\eta_{\text{Carbon}} = \left(1 - \frac{m_{\text{C,TOC}}}{m_{\text{C,Fuel}}}\right) * 100 \text{ (Eq. 2)}$$

In the above equation,  $\eta_{\text{Carbon}}$  is the carbon conversion efficiency,  $m_{\text{C, Fuel}}$  is the mass flow rate of fuel C and  $m_{\text{C,TOC}}$  is the mass flow rate of GL TOC, which is almost entirely present in the dissolved filtrate alone. The TOC fraction is believed to be composed of ionic and polar, likely low-molecular weight species soluble in water at the operating conditions (30 bar, pH ~ 12) encountered in the GL dissolver.

## 4.2 Thermodynamic Equilibrium Calculations of Black Liquor Gasification

(Paper III)

The capability of TECs to predict product compositions and gasification performance indicators for BLG is evaluated by validating predicted results against pilot-scale experimental data. In order to

better understand the underlying reasons behind the discrepancies between predicted and measured results, the sensitivity of TEC predictions to variations in input data is also examined.

**Table 5. Components in SIMGAS database.**

Gas	Solid/Liquid
<sup>a</sup> H <sub>2</sub> (g)	<sup>b</sup> Na <sub>2</sub> CO <sub>3</sub> (l)
<sup>a</sup> CO (g)	<sup>b</sup> Na <sub>2</sub> S (l)
<sup>a</sup> CO <sub>2</sub> (g)	<sup>b</sup> NaCl (l)
<sup>a</sup> H <sub>2</sub> O (g)	<sup>b</sup> NaOH (l)
<sup>a</sup> H <sub>2</sub> S (g)	<sup>b</sup> Na <sub>2</sub> SO <sub>4</sub> (l)
<sup>a</sup> CH <sub>4</sub> (g)	<sup>b</sup> K <sub>2</sub> CO <sub>3</sub> (l)
<sup>a</sup> COS (g)	<sup>b</sup> K <sub>2</sub> S (l)
<sup>a</sup> N <sub>2</sub> (g)	<sup>b</sup> KOH (l)
	<sup>b</sup> KCl (l)
	<sup>b</sup> K <sub>2</sub> SO <sub>4</sub> (l)
	<sup>a</sup> C (s)

<sup>a</sup> From NIST Chemistry WebBook.

<sup>b</sup> From Lindeberg [122].

TECs are carried out using a MATLAB-based in-house tool called SIMGAS, which is based on a non-stoichiometric approach that works by minimizing the Gibbs free energy of the reacting system using an active-set method to include both linear and non-linear constraints. Compared to a more established commercial package like FactSage (GTT-Technologies, Germany), SIMGAS uses a simpler thermodynamic model in which the gas and the molten inorganic phases are represented by ideal mixtures of components. The components in the gas and solid/liquid databases on SIMGAS are listed in Table 5. The choice of the components for inclusion in the databases is based on analysis of experimental measurements under various process conditions.

A number of OPs were simulated in both FactSage and SIMGAS to establish whether the latter was fit for purpose. The results of the comparison are detailed in the Supplementary Material for Paper III. Significant differences were not observed for major species and SIMGAS was deemed to be adequate for the purpose of the study. SIMGAS was chosen ahead of FactSage as it was easier to implement constraints for known deviations from equilibrium, such as in the case of CH<sub>4</sub> and H<sub>2</sub>S. With a significantly larger set of solution databases, FactSage would have been a more appropriate choice if the aim had been to study smelt properties or the interactions between reactor walls and smelt [123].

#### 4.2.1 Dataset for Validation of TEC Predictions

The dataset for validating TEC predictions was assembled from three experimental studies, which are summarized in Table 6. In Furusjö et al., 2014, STL is used as a feedstock, which differs from kraft BL in some important aspects that are discussed in more detail in Paper III. The study by Jafri et al., 2016 constitutes Paper I in this work. Note that the reactor temperatures presented in Paper I differ from those used in the TEC comparison in Paper III by 10–20 C. This is because the original

experimental study only presented temperature readings from one of the two mid-level thermocouples whereas the comparison with TEC results was carried out using an average value.

**Table 6. Description of datasets for TECs of black liquor gasification (taken from pilot-scale studies).**

Study	Feedstock	Number of OPs <sup>a</sup>	Feed Input [MW <sub>th</sub> HHV]	Pressure [bar g]	Notes
Jafri et al., 2016 [Paper I]	Kraft Black Liquor	5	2-6-3.1	24-29	See Table 2 and the accompanying discussion.
Wiinikka et al., 2015 [88]	Kraft Black Liquor	6	3	25-29	Besides pressure, $\lambda$ was also varied.
Furusjö et al., 2014 [69]	Sulfite Thick Liquor	8 <sup>b</sup>	2.5-3.3	27-29	OPs were designed to assess the quality of green liquor at high feed rates.

<sup>a</sup> Operating Points.

<sup>b</sup> OP2 in the original dataset was excluded from TECs on account of exceptionally poor mass balance closure.

#### 4.2.2 Simulation Details

Besides relevant thermodynamic data and assumptions, the input to the TECs of BLG consists of the flow rates, pressures, temperatures and compositions of the streams that flow into the gasification reactor, the heating value of the feedstock and the loss of heat through the reactor walls. Three streams enter the BLG reactor: pulping liquor, oxygen and nitrogen. Compared to the other flows, the nitrogen flow is very small. In the pilot-scale experimental studies used for validation, the mass flows of oxygen and pulping liquors are measured with Coriolis type mass flow meters, which have manufacturer specified measurement errors of 0.2%. Experience shows that greater uncertainty can be expected in practice and a 95% confidence interval of  $\pm 1\%$  is used instead.

BLG is an autothermal process, which means that the heat required by gasification reactors is generated by partial oxidation of the feedstock inside the gasification reactor itself and temperature is regulated by the amount of added oxygen. For the comparison with experimental data, TECs were set up to calculate equilibrium temperature by solving an energy balance over the reactor. The enthalpies of the streams entering and leaving the reactor were defined with respect to the standard enthalpy of formation, which is readily available in the literature for components like oxygen, nitrogen and gaseous products, the chemical compositions of which is well known. However, STL and kraft BL are both complex mixtures of organic and inorganic species without ready availability of standardized data.

The value of the standard enthalpy of formation of STL and kraft BL was computed by applying Hess' law to their respective combustion reactions and determining reaction enthalpies by bomb calorimetry. In order to do this, knowledge of the final product composition in the bomb calorimeter is needed. An investigation into calorimetry remains (see Supplementary Material for Paper III) found that, contrary to the assumptions typically used for low-ash feedstock, carbon ends up as a mixture of carbon dioxide and sodium carbonate, while sulfur ends up as sodium sulfate or sodium hydrogen sulfate depending on the sodium/sulfur ratio.



In this work, the predicted concentrations of the inorganic components in smelt are compared with experimentally obtained concentrations of inorganic components in GL, which is formed of smelt dissolved in water. The principle components in smelt are carbonate, sulfide and hydroxide. In GL, they are carbonate, sulfur and TIC (total inorganic carbon). TIC is the sum of carbon present as carbonate and hydrogen carbonate, which is not present in the smelt as it exits the reactor but is formed during the subsequent quenching process. According to both TEC predictions and experimental data, sodium and potassium are found solely in GL. The differences between predicted smelt compositions and experimental measured GL compositions are discussed in Chapter 5.2.1.

### 4.3 Techno-Economic Evaluation of Biofuels from Kraft Black Liquor

(Papers IV, V and VI)

The economic viability of biofuels from kraft BL is evaluated using two contrasting approaches within the techno-economic methodology framework. Six different pathways are studied, which are listed in Table 7 together with the economic performance indicator(s) used in their evaluation.

**Table 7. List of pathways included in the evaluation of the economic case for biofuel synthesis from kraft black liquor. See the text in Chapter 4.3.3 for definitions of the economic performance indicators.**

Pathway	Economic Performance Indicator			Paper
	Profitability <sup>a,b</sup>	Breakeven Plant/Investment Size <sup>c</sup>	Minimum Fuel Selling Price <sup>d</sup>	
BLG-MeOH	✓	✓	×	V
BLG-PTRL	×	×	✓	VI
EL-BLG-PTRL	×	×	✓	VI
CO-BLG-PTRL	×	×	✓	VI
MSL-HDO	✓	✓	✓	V, VI
MSL-HDO-EL	×	×	✓	VI

<sup>a</sup> See Chapter 4.3.3 for detailed descriptions of each indicator.

<sup>b</sup> A biofuel pathway is defined as being profitable if the specific margin for investment in a given energy market scenario exceeds its annualized specific investment cost.

<sup>c</sup> The minimum plant and investment sizes for which the specific margin for investment for a biofuel pathway exceeds its annualized specific investment cost. The scaling approach used is simplistic and the results are meant to be indicative.

<sup>d</sup> The selling price of biofuels at which the net present value of an investment is equal to zero given a capital recovery factor of 0.1.

In all but one of the pathways the production of biofuel is co-located and integrated with both a pulp mill and a crude oil refinery. Detailed process spreadsheet models based on best available experimental results are used to generate product yields and energy performance data.

#### 4.3.1 Selected Evaluation Approaches

When evaluating the economic viability of a technology pathway for biofuel production, it is typically the case that a minimum fuel selling price (MFSP) is calculated using discounted cash flow rate of return analysis, which enables a direct comparison with fossil and other renewable alternatives. In using the above approach, it is assumed that technical performance data in industrially relevant scale is in existence and that reasonably accurate capital expenditure estimates

can be assembled with a degree of confidence compatible with the expected accuracy range of the analysis. As noted in Chapter 1.4, the industrially relevant alternatives for the production of biofuels from kraft BL are at different stages of technology development. Representative data for critical parameters, such as product yields and process energy efficiencies is often hard to find in the open literature. Equally problematically for economic evaluations, capital cost estimates for the less developed pathways are generally not only more opaque but also subject to a greater degree of uncertainty. The provision and disclosure of de-aggregated data, such as component-level cost breakdowns is also impacted by considerations of commercial sensitivity.

Hence, an alternative approach that treats uncertain CAPEX estimates in a more qualitative manner when determining profitability is used to evaluate the production of high blend and drop-in biofuels from kraft BL in Paper V. The two relevant kraft BL-based routes are represented by the BLG-MeOH and MSL-HDO pathways, which are compared with other industrially relevant forest-based alternatives. The main indicator of economic performance is *profitability*. In addition, economic performance is also examined using the concept of “breakeven points” to explore the trade-off between economies-of-scale and the willingness to mobilize sufficient capital as the high initial capital costs of biorefineries have been identified as an economic risk factor that can block or delay investments. More details on the approach can be found in Section 2.3 of Paper V.

The results of the multi-aspect evaluation in Paper V informed the design of the study presented in Paper VI, which approaches the economic viability of biofuel production from the perspective of the pulp mill and investigates whether relatively small lignin separation or BL gasification units that utilize only a part of the BL available at a given mill can be used to produce economically competitive drop-in biofuels. One of the more industrially relevant pathway for the above purpose is MSL-HDO, which has witnessed an increasing number of process steps undergo technology development in the recent past. Although significant uncertainty still exists, an improvement in the quality of technical and cost data means that MFSP is used as the indicator of economic performance in the evaluation in Paper VI.

### 4.3.2 Energy Performance Indicators

Depending on where the system boundary is drawn, the energy efficiency of a process can vary significantly. To illustrate the importance of the systems perspective and to facilitate consistent comparisons based on the same assumptions, two measures of energy efficiency that reflect different boundaries are defined below.

An overall system efficiency  $\eta_{\text{system}}$  is defined in eq. 3 as the ratio of the energetic value of biofuel products to the energetic value of all primary energy inputs. Only net flows are considered. In addition to BL and BL lignin, other primary energy inputs are hydrogen, electricity and PO.

$$\eta_{\text{system}} = E_{\text{Product}} / E_{\text{Primary-Inputs}} \text{ (Eq. 3)}$$

In the definition for  $\eta_{\text{system}}$  given above, the system boundary is drawn around the biofuel production process. The integration of biofuel production units with the mill and the refinery results in changes to overall material and energy balances. The effect of integration on energy performance can be quantitatively assessed using the concept of expanded system efficiency.  $\eta_{\text{system-exp}}$  is defined in eq. 4 as the ratio of the energetic value of the biofuel product to the net energetic value of integrated/expanded energy inputs.

$$\eta_{\text{system-exp}} = E_{\text{Product}} / E_{\text{Expanded-Energy-Inputs}} \text{ (Eq. 4)}$$

Under the expanded system perspective, the feedstock to the biofuel production process is not BL or BL lignin but the net change in mill biomass and electricity balance from the integration of biofuel production. In an analogous fashion, the net change in refinery natural gas and electricity balances constitutes a secondary input. Listings of energy inputs to efficiency calculations are provided in Table 2 of Paper IV and in Table 4 of Paper VI. Information on the evaluation of gasifier performance using other efficiency measures can be found in Paper IV.

### 4.3.3 Economic Performance Indicators

All prices and cost estimates used in the economic evaluations are adjusted for inflation, where appropriate, before being converted to 2017 EUR using exchange rates of 9.5 SEK/EUR, 8.5 SEK/USD and 10.5 SEK/GBP.

#### Profitability (Paper V)

The profitability of a given biofuel pathway is determined by examining whether its *specific margin for investment* exceeds its *annualized specific investment cost*. The *specific margin for investment* is a measure of the income available for covering capital costs on a yearly basis. It is calculated from the balance of revenue and expenditure in units of EUR/MWh. Three different energy market scenarios are examined in Paper V, which each yield a different *specific margin for investment*. The energy prices for a 2018 energy market scenario are given in Table 8. The prices of consumables such as catalysts and chemicals that did not vary between scenarios are listed under Appendix C in the Supplementary Material for Paper V. A sensitivity analysis is also performed to assess the effects of selected cost and performance-related uncertainties on specific investment margin in the 2018 energy market scenario (Table 3 in Paper V).

The *annualized specific investment cost* is calculated using an annuity factor of 0.15, based on an internal rate of return of 15% and an estimated plant life of 20 years. The annuity is applied to available CAPEX estimates from the literature that are converted to units of EUR/MWh assuming an on-stream factor of 0.95. An operations and maintenance supplement, set at 4% of the specific investment cost is also included. The CAPEX estimates used to calculate *annualized specific investment costs* are detailed in Tables 6-8 in Paper V.

**Table 8. Energy prices in Papers V and VI.**

[EUR/MWh]	Paper V <sup>a</sup>	Paper VI <sup>a</sup>
Bark	n/a	15
Forestry residues	20	19
Heating oil [E <sub>10</sub> /EO <sub>1</sub> ]	39	n/a
Natural gas	35	45
Ethanol [T <sub>2</sub> ]	85	n/a
Methanol	85	n/a
HVO diesel	75	n/a
Fossil diesel	37	n/a
Fossil petrol	49	n/a
Hydrogen	42	54
Electricity (purchased)	33	34
Electricity (sold)	30	32
Pyrolysis oil	n/a	76

<sup>a</sup>See Table 2 in Paper V and Table 5 in Paper VI for sources and detailed notes.

### **Breakeven Plant & Investment Size (Paper V)**

A breakeven plant & investment size for each pathway is determined by scaling the total capital investment (TCI) estimates with a uniform scale exponent until the *annualized specific investment cost* exceeds the available *specific margin for investment*. As several key technologies are still under development, the evaluated pathways are likely to benefit from technology learning. Hence, a distinction is drawn between FOAK and nth-of-a-kind (NOAK) investment estimates. Since the underlying cost estimates contain large uncertainties, the breakeven points are meant to be purely indicative of the smallest scale, both in terms of plant and investment size, at which a given pathway could be economically viable under the chosen assumptions.

### **Minimum Fuel Selling Price (Paper VI)**

The MFSP of biofuels for the pathways evaluated in Paper VI is determined by discounted cash flow rate of return analysis. MFSP is defined as the biofuel selling price that makes the net present value of an investment equal to zero for a capital recovery factor of 0.102, which is given by a real discount rate of 8% compounded annually over 20 years. The capital cost estimates are treated as n<sup>th</sup> plant costs, while the operations and maintenance cost is fixed at 4% of TCI inclusive contingency. An availability factor of 90% is applied to all pathways and the rate of biofuel production is assumed to be constant over the lifetime of an investment. In all the pathways evaluated in Paper VI, the first step in the conversion process, namely gasification (up to and including methanol distillation) and lignin separation, respectively, is sized to equal 18.5% of the BL flow to the RB on an energy basis (HHV) for each of the three mills, which all have different BL throughputs. The refinery-based units, namely the hydrotreater and the MTG plant are sized to take advantage of economies-of-scale.

However, in the economic evaluation, the cost is split up in a manner that, for a given mill the fraction of cost borne by the pathways is in proportion to the size of the gasification/lignin separation unit.

For each component, a breakdown of TCI by cost component is provided in Section B<sub>1</sub> of the Supplementary Material for Paper VI. In most cases equipment costs are based on commercial estimates of engineering, procurement and construction costs (gasifier, water-gas shift, amine wash, methanol synthesis and distillation, gasification and catalytic synthesis balance of plant) or lump sum total overnight investment costs (lignin separation and upgrading, hydrotreater rebuild). The investment cost for the MTG unit is taken from the literature as total overnight investment cost. The specific (installed) investment cost of PEM electrolyzers is set at 1500 EUR/kW. Cost projections for PEM electrolyzer systems vary considerably in the literature, sometimes owing to confusion over inclusion of installation costs. The contingency level for the electrolyzer is set at 30% of total direct costs, partially to mitigate against the risk of cost underestimation. The performance of the PEM stack degrades over the lifetime of the electrolyzer. It is assumed that the stack is replaced once over the economic lifetime of the investments, which is an optimistic assumption. Stack replacement cost is set at 60% of installed equipment cost and included in the calculation as an annualized operating costs applicable for the lifetime of the investment [124].

#### **4.3.4 Process Modelling for Techno-Economic Evaluation**

A detailed spreadsheet model that took into account the effect of biofuel production on mill and refinery balances was prepared for each pathway. Relevant process data, such as temperatures, pressures, yields and product compositions were taken from the open literature and supplemented with information from technology developers and subject matter experts. The integration points between the mill and refinery on the one hand and the biofuel production units on the other hand differ somewhat between lignin separation-hydrotreatment and BL gasification-catalytic synthesis. In general, there is an exchange of steam, electricity, the alkaline cooking chemicals and fuel gases with the mills, and of heat and fuel gases with the refinery. The size of the biofuel unit relative to the amount of BL produced at the mill also plays a role in determining the direction of the exchange. A summary of important modeling assumptions, and key energy and material exchanges with the pulp mill and the refinery is provided below for each pathway. See Section 3.1 in Paper IV and Section 3.2 in Paper VI for more details on material and energy integration.

##### **BLG-MeOH**

The process model for biofuel production in BLG-MeOH is the same as the one described by Carvalho et al. [77]. In BLG-MeOH the RB is substituted for a gasifier. The effect on the energy balance is significantly different if the RB is retained and only a part of the BL is upgraded to methanol as is done in Paper VI (not shown).

## BLG-PTRL

The gasifier is modelled in SIMGAS, which is introduced in Chapter 4.2. TECs calculate the amount of oxygen required to reach a temperature of 1050°C by solving an energy balance over the gasifier. The equilibrium composition of syngas and slag is obtained as the output. TECs are mill specific, as the composition of BL is different for different mills. The concentration of CH<sub>4</sub> in syngas was fixed at 1 mol%, based on experimental measurements. H<sub>2</sub>S is determined by an empirical modification to the thermodynamic model. Heat loss through the reactor walls is set at 0.7% of the feedstock energy input, which varied between 505-510 MW HHV. The results generated by the TECs are considered scalable within the biofuel production range evaluated in the study. The upgrading of syngas to methanol is modelled in Aspen Plus™ 8.4. In the first step in the model syngas is cooled to a temperature of 40°C and the heat recovered is used to produce hot water at 90°C and saturated low pressure steam at 4 bar.

To meet the stoichiometric requirement for methanol synthesis, the modulus of syngas is adjusted from approximately 1-1.1 to 1.95 by mixing it with saturated intermediate pressure steam (30 bar) in a water gas shift unit that is modeled as an equilibrium reactor. The water gas shift unit also consumes small amounts of electricity. Since water gas shift is moderately exothermic, there is an increase in syngas temperature, which is exploited to generate some intermediate pressure (10 bar) and low pressure (10 bar) steam. Afterwards, CO<sub>2</sub> and H<sub>2</sub>S are removed from syngas in an amine wash, which consumes small amounts of electricity and large amounts of low pressure steam to regenerate the amine. The concentration of CO<sub>2</sub> in syngas exiting the acid gas removal unit is set at ~ 3 wt.%. Since the addition of the ZnO bed to the process has minimal impact on the overall energy balance, it is excluded from the Aspen Plus model.

Methanol synthesis is modeled as an equilibrium reactor operating at 254°C with a temperature approach of 30°C, an inlet pressure of 90 bar and a pressure drop of 5.5 bar across the methanol loop. Since the synthesis reactions are exothermic, isothermal conditions in the reactor are maintained by continuously removing heat, which is utilized to produce saturated intermediate pressure steam at 30 bar. Large amounts of water are also produced. The unconverted gas is recycled back to the reactor by mixing it with fresh syngas feed. The combined feed is pre-heated to the required reactor inlet temperature by heat exchange with the effluent, which is further cooled with water to separate raw methanol from the mix of unconverted gases by condensation. It is assumed that the raw methanol out of the synthesis unit is “stabilized” to a purity of 96%. The energy for the stabilization is supplied by low pressure (4 bar) steam. Sources in the literature indicate that the MTG process can handle methanol feeds with a purity of 96% [113], [125].

MTG yield structure is taken from an MTG process simulation by Larson et al., 2012. They assumed that the dehydration of methanol to DME takes place at equilibrium, which is seen as a good approximation to reality [126]. For the MTG reaction, they assumed a product yield structure based

on Barker et al. and Schreiner [127], [128] and found good agreement with aggregate product distributions reported by Zhao, et al. [113] in Table 3 of their study. In the study presented in Paper VI it is assumed that 75% of the waste heat recovered from the process is used internally, while the remainder is exported to the refinery, where it displaces an equivalent amount of energy from natural gas. The electricity consumption of the MTG process is assumed to be negligible.

#### **EL-BLG-PTRL**

EL-BLG-PTRL shares most process steps with BLG-PTRL and is modelled similarly. The exceptions are discussed below. The water gas shift unit is not included in the model. Instead, CO<sub>2</sub> concentration in syngas is reduced to ~ 3 mol% in the amine wash and H<sub>2</sub> is added to syngas in amounts that yield a modulus of 1.95 in the feed to methanol synthesis. The PEM electrolyzer used for the production of H<sub>2</sub> is assumed to have an electricity-to-product efficiency of 80% on an HHV basis. The O<sub>2</sub> produced by the electrolyzer is supplied to the gasifier, which significantly reduces the import requirement.

#### **CO-BLG-PTRL**

The spreadsheet model for CO-BLG-PTRL is the same as for BLG-PTRL. The two pathways differ only in feedstock composition, which impacts syngas composition and biofuel yield but the underlying modelling assumptions remain the same.

#### **MSL-HDO**

The spreadsheet model for lignin extraction and lignin hydrotreatment was based on mass and energy balance data provided by SunCarbon AB in both Paper IV and VI. The model in the latter paper was based on an updated configuration and more granular, better quality data. The inorganic and the non-lignin organic fractions in weak BL are eventually returned to the evaporation plant. The sulfuric acid used for washing the lignin product is also returned to the mill. Other points of integration between the biofuel unit and the mill include the use of intermediate pressure (30 bar) and low pressure (4 bar) steam for heat treatment and purification, respectively, and the combustion of the sulfur-rich gases released during the separation of lignin in the RB.

The upgrading of lignin to petrol and diesel blendstock is handled somewhat differently in Papers IV and VI. An indirect method is used in both instances to model lignin hydrotreatment as pilot-scale experimental data on product yields is unavailable in the literature. The consumption of hydrogen and the product structure in the hydrotreatment step are estimated from lab-scale experimental data on the upgrading of lignin esterified with tall oil fatty acid and light gas oil in Paper IV [129]. The approach used is described in greater detail in Section 4.1.1 in Paper IV. Hydrogen is supplied from an existent onsite natural gas reformer. During normal operation, the heat demand of the model refinery is met by combusting heating oil. It is assumed that the energy gases released during hydrotreating of bio-oils can replace an equal amount of heating oil in the furnace, and that

any process heat recovered can also do so with a ratio of 4:5 on an energy basis, i.e. with a theoretical boiler efficiency of 80%.

In Paper VI an improved model of the refinery is evaluated. Hydrogen consumption and lignin yields were calculated from experimental data on the hydrotreatment of light light gas oil, renewable tall diesel and a 10/60/30 lignin/light light gas oil/renewable tall diesel blend. See Section 3.2.1 in Paper VI for more information. The heat demand of the model refinery is met by combusting natural gas, which is replaced with heat and natural gas from the hydrotreatment of lignin with a ratio of 1:1 on an energy basis. Experiments investigating the hydrotreatment of VGO/lignin blends in the two-step iso-cracker are currently underway and it is likely that more representative data on lignin yields will be available in the very near future.

### **MSL-HDO-EL**

The energy balance model for MSL-HDO-EL is largely same as for MSL-HDO. The two pathways differ only in the source of hydrogen for hydrotreatment. In the -EL variant, hydrogen is produced by PEM electrolysis of water with an electricity-to-hydrogen efficiency of 80% (on HHV basis).

## **4.4 Evaluations of Other Performance Aspects**

(Papers V and VI)

In addition to energy performance, profitability and production cost, three other aspects that can influence the economic viability and commercial deployment of biofuel technologies are evaluated: (i) Technology maturity, (ii) GHG performance, and (iii) Biofuel production potential.

### **4.4.1 Technology Maturity**

The TRL scale employed by the European Commission for the Horizon 2020 program is used as the basis for evaluating the technology maturity of the studied pathways [109]. The TRL framework is a useful and well-established tool for monitoring and comparing technology development [130]. According to the Commission's definition a TRL of 1 indicates the knowledge of basic principles only, while a TRL of 9 denotes proven operation in commercial scale. The vagueness of these definitions, which are intended for a broad audience makes it challenging to carry out a more finely grained assessment. To improve analysis precision, a set of more topical and quantitative definitions from the US Department of Energy is used as an additional source of guidance [131].

Since the pathways evaluated in this thesis include a mix of technologies at different stages of development, two distinct but complementary approaches for TRL estimation have been used based on the definitions discussed above: (a) the weighted average approach, (b) the weakest link approach. Process configurations are broken down into 3-6 smaller steps. Integration with existing industrial facilities is treated as a fully-fledged separate step. Each process step is assigned an



individual score. In the weighted average approach, the overall TRL is determined by assigning each step a weight based on complexity and criticality. In the weakest link approach, the lowest TRL score among the steps with a weight greater than 0.2 is chosen as the overall TRL score.

#### 4.4.2 GHG Performance

GHG footprints are estimated using a simplified approach based on RED guidelines [30]. It has been shown that the bulk of the climate impact of lignocellulosic biofuels is attributable to feedstock supply, electricity and H<sub>2</sub> [62], [92], [132], [133]. The emission factors used as inputs, which are selected in accordance with the aforementioned findings are shown in Table 9.

**Table 9. Emission factors for GHG footprint assessments.**

Input	GHG footprint [gCO <sub>2</sub> eq/MJ LHV]	Comments [Source]
Forest residues	2.2	Emissions associated with “typical” technology and transport distance. All pathways except 1-MSL-HDO. [134]
Hydrogen	91.4	From steam reforming of natural gas. Hydrotreatment (1, 3a-c) pathways only. [135]
Electricity	13.1	Swedish electricity mix in accordance with Swedish Energy Agency recommendation. All pathways. [136].
Heating oil	80.0	Based on the reference value for heat production in the proposed RED II directive. 1-MSL-HDO, 3a-Pyr-HDO, 3b-Pyr-FCC only. [137]
Petrol	93.5	Used in the system expansion for 3b-Pyr-FCC only. [137]
Diesel	95.5	Used in the system expansion for 3b-Pyr-FCC only. [137]

#### 4.4.3 Biofuel Production Potentials

Estimates of feedstock potentials and assessments of processing constraints are used in conjunction with biofuel-to-biomass conversion efficiencies to assess the production potentials of biofuels from BL [138]–[140]. Feedstocks potentials are presented as a range with upper (optimistic) and lower (conservative) estimates in Table 5 of Paper V. The upper estimate for BL assumes an annual production increase of 1.3% up to the year 2030 and supposes that all of the BL in all of the Swedish kraft pulp mills is available for biofuel production. The lower estimate only considers current production from mills home to RBs built before 1995. The upper estimate for lignin takes the upper estimate for BL and assumes that 30% of the lignin present can be extracted. The lower estimate is built on mill-specific appraisals of maximum extraction potential as different mills are likely to have different maximum extraction thresholds [139].

## 5 Results & Discussion

*This chapter presents and discusses research results. The first sub-chapter focuses on research question 1, which concerns the gasification performance of black liquor and pyrolysis oil blends in pilot-scale experiments. The second sub-chapter is addressed to research question 2, which concerns thermodynamic equilibrium calculations of black liquor gasification. The third sub-chapter is written in response to research questions 3 and 5, which concern the economics of biofuels from black liquor. The fourth and final sub-chapter deals with the evaluation of other relevant performance aspects raised in research question 4.*

### 5.1 Pilot-Scale Gasification of Pyrolysis Oil & Black Liquor Blends

In response to research question 1, this subchapter presents selected results from Papers I and II that show how blending kraft BL with up to 20 wt.% PO impacts on gasification performance indicators described in Section 4.1.5. A discussion on mass and energy balance closures, which are used to establish the reliability of the underlying experimental data is also provided.

#### 5.1.1 Syngas Quality and Cold Gas Efficiency

The effect of blending kraft BL with up to 20 wt.% PO on syngas yields is illustrated in Figure 6. Changes in the molar flow rates of major syngas species are plotted as a function of feedstock alkali-to-carbon ratio for selected OPs with the same thermal load of ~2.75 MW (see Table 2). Increasing the fraction of PO in the blends results in an increase in the yield of CO at the expense of CO<sub>2</sub>, while the yield of H<sub>2</sub> is relatively unaffected. As a consequence, the H<sub>2</sub>/CO ratio in syngas sees a small reduction from a value of 1.36 for unblended BL to 1.24 for a 20/80 PO/BL blend. Since the inorganic content in BL acts as a thermal ballast in the reactor, an increase in PO fraction means that less heat is required to bring reactor contents to gasification temperature, thus resulting in reduced consumption of CO and H<sub>2</sub>.

The improvement in energy performance resulting from the blending of kraft BL with PO can be clearly traced in Figure 7, which shows a plot of different measures of energy efficiency as a function of alkali-to-carbon ratio. The 20/80 PO/BL blend has a 7%-point higher CGE<sub>Power</sub>, a 7%-point higher CGE<sub>Fuel</sub> and a 5%-point higher CGE<sub>Fuel+S-free</sub> than unblended BL.

The effect of reactor temperature on the yields of major syngas species from unblended BL and a 15/85 PO/BL blend is shown in Figure 3a of Paper II. The composition of major gas species varies in largely the same way in response to changes in gasification temperature for both feedstocks, which indicates that their gasification behavior is relatively similar. The potential for methanol production peaks at a methane concentration ~1% for a 15/85 PO/BL blend as seen from Figure 9 in Paper II. At

the higher temperature setting denoted by a methane content of ~2%, there is a drop in  $CGE_{Fuel}$ , which is likely caused by the oxidation of CO to  $CO_2$ .

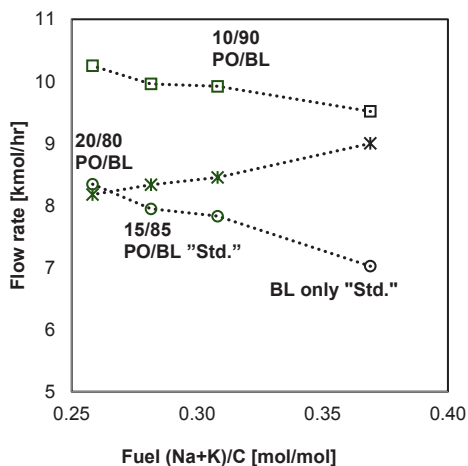


Figure 6. The change in the yields of CO (circle),  $CO_2$  (star) and  $H_2$  (square) in response to an increase in the fraction of PO in the blends at the same approximate thermal load and methane content.

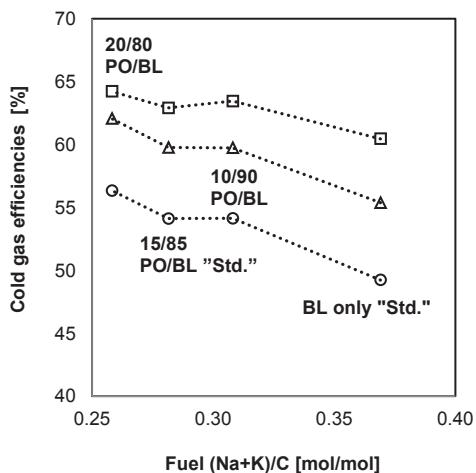
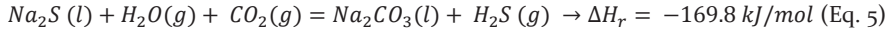


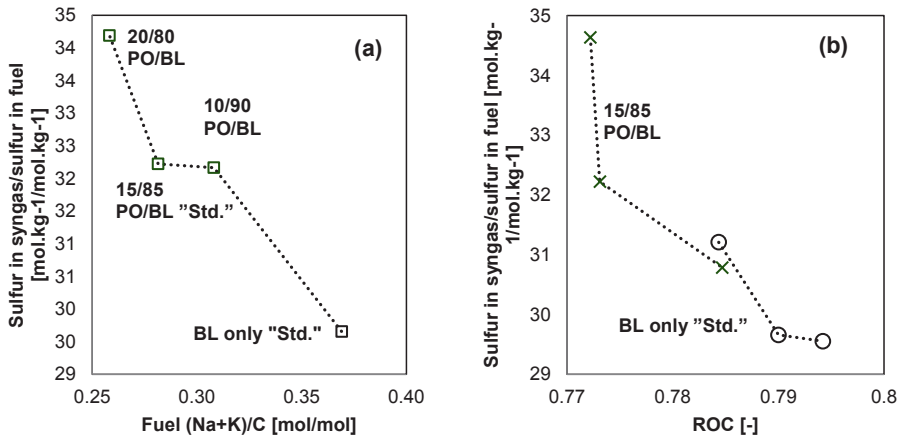
Figure 7. The change in  $CGE_{Fuel}$  (circle),  $CGE_{Power}$  (triangle) and  $CGE_{Fuel+S-free}$  (square) in response to an increase in the fraction of PO in the blends at the same approximate thermal load and methane content.

As a consequence of the sulfur split (see Chapter 4.1.5), some of the feedstock sulfur can be recovered separately in a relatively easily upgradable gaseous stream. Figure 3b in Paper II shows that the

decrease in blend sulfur content with increasing PO fraction results in a corresponding decrease in the amount of sulfur released as  $H_2S$ . At the same time, the split also promotes the formation of alkali carbonates in GL, which leads to an increase in the consumption of burnt lime in the causticisation unit at the mill as discussed in the next subchapter. Sulfur split is plotted as a function of feedstock alkali-to-carbon ratio in Figure 8a, which shows that approximately one third of feedstock sulfur ends up in syngas. There is a downward trend with increasing PO fraction. It is likely that the change in the yield of the major components with changing PO fraction also impacts on the partial equilibrium of the reaction governing the sulfur split, given in eq. 5.



The results presented in Figure 8 run contrary to TEC predictions, which typically find nearly two thirds of the feedstock sulfur in gas phase at the operating conditions encountered in BLG [87]. It therefore seems clear that while eq. 5 may reach a partial thermodynamic equilibrium, the division of feedstock sulfur between smelt and syngas is determined in the main by kinetic limitations.



**Figure 8.** The change in sulfur split in response to (a) an increase in the fraction of PO in the blends at the same approximate thermal load and methane content, and (b) an increase in temperature (with increasing relative oxygen content value, see Section 4.1.5 for a definition) at the same approximate thermal load for unblended BL (circle) and a 15/85 PO/BL blend (cross).

The effect of reactor temperature on the sulfur split of unblended BL and a 15/85 PO/BL blend is illustrated on Figure 8b. The fraction of feedstock sulfur that ends up in syngas decreases by 2-4%-point over the studied temperature range for both feedstocks. This is expected from Le Chatelier's Principle as an increase in reactor temperature favors the formation of  $Na_2S$  at the expense of  $H_2S$ , but the extent of the shift is likely limited by the fact that the reaction in eq. 5 only attains partial thermodynamic equilibrium. Note that some COS was also found in syngas samples but the

measured concentrations were below 100 ppm<sub>v</sub>. Since an unknown amount of COS is hydrolyzed to H<sub>2</sub>S during syngas cooling, it was not possible to identify how changes in feedstock composition influenced COS concentrations in the gasification reactor.

Syngas from PO/BL blends was, in general, as clean as that from unblended BL. The only higher hydrocarbon specie present in concentrations greater than 20 ppm<sub>v</sub> was benzene, which was limited to concentrations below 100 ppm<sub>v</sub> in examined syngas samples. Figure 4 in Paper I shows that changes in the concentrations of methane and benzene from unblended BL follow a similar pattern in response to changes in operating conditions. Figure 6 in Paper II shows a similar correlation for a 15/85 PO/BL blend.

### 5.1.2 Green Liquor Quality and Carbon Conversion Efficiency

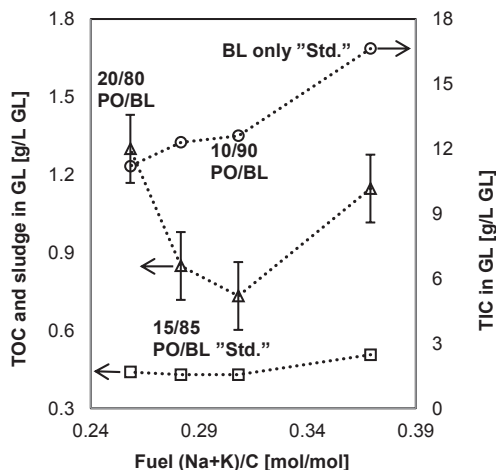
The concentrations of the most important ions and elements in the GL from unblended kraft BL are presented in Table 3 of Paper I. A similar set of information for the GL from PO/BL blends with up to 20 wt.% PO is provided in Table 4 of Paper II. As a point of reference, the equivalent data for GL from a typical kraft RB is also provided in the first of the two above-mentioned tables.

GL from BLG differs from GL from RBs in a few aspects. First, typical RB GL contains hydroxide ions, which are not present in BLG GL as they react with the CO<sub>2</sub> in syngas to form bicarbonate ions. Second, in BLG some of the sulfur enters the gas phase as discussed in the previous subchapter, thereby resulting in an increased concentration of carbonate ions in the GL as per eq. 4. As a consequence of the above, BLG GL has a higher TIC content than RB GL, which leads to an increase in the consumption of burnt lime in the causticisation unit at the pulp mill. Based on Table 3 in Paper I, the increase amounts to 31-55% for GL from the gasification of unblended kraft BL at different settings. The increase is somewhat smaller for the blends as the fraction of sulfur in gas phase undergoes a marginal reduction with increasing PO fraction. A syngas cooling setup that is designed to minimize CO<sub>2</sub> absorption can help mitigate the increase to some extent.

The effect of blending kraft BL with up to 20 wt.% PO on the concentrations of GL TOC, TIC and sludge is plotted in Figure 9 as a function of feedstock alkali-to-carbon ratio for the same OPs as in Figure 6. It can be seen that the vast majority of carbon in GL is present in dissolved form as TIC. As expected and touched upon earlier, the TIC content of GL decreases with increasing PO fraction. GL sludge is largely composed of insoluble inorganic salts that are unaffected by changes in operating conditions and feedstock compositions in the ranges considered. The fraction of carbon in sludge does not exceed 8% in the studied samples. ~

GL TOC content for the OPs shown on Figure 9 is in the range 0.7 to 1.2 g/L, which is comparable to the ~1 g/L found in typical RB GL. Concentrations up to 1.8 g/L have been measured in other experiments at the pilot plant. TOC content has a relatively high estimated measurement uncertainty of 15% but the magnitude of the variations between the OPs exceed the span of the

experimental error bars. GL TOC does not vary systematically with feedstock composition (Figure 9) or temperature (not shown). The carbon conversion efficiencies, which are calculated from GL TOC measurements are in the range 98.8-95.5% of all the OPs in Table 2. Systematic variations with either blend ratio or temperature have not been encountered. A very high degree of carbon conversion is also indirectly supported by the absence of visually detectable unconverted char in GL samples from both unblended BL and PO/BL blends.



**Figure 9.** The change in total inorganic carbon (TIC, circle), total organic carbon (TOC, triangle) and sludge (square) in response to an increase in the fraction of PO in the blends at the same approximate thermal load and methane content.

It can be seen from Table 4 in Paper II that the measured concentrations of sulfide ions were lower than the measured concentrations of total sulfur. At the same time, the correlation coefficient between the two measures was 0.90, which suggests that the measurements are relatively accurate. In an earlier study, sulfur reduction efficiencies of 100% within measurement uncertainty limits have been reported [69]. For comparison, efficiencies for typical RB GL are usually in the range 90-95%. The methods used for measuring sulfide and total sulfur concentrations have specified relative measurement uncertainties of 15% and 10%, which are of the same order of magnitude as the disagreement itself (10-30% relative to sulfide). GL is extremely sensitive to oxidation during sample preparation, which means that establishing the concentrations of reduced forms of sulfur in actual reaction conditions is specially challenging. Given the previous recorded high sulfur reduction efficiencies and the large experimental uncertainties in the measurement methods, there is a possibility that the deviation is down to analysis-related errors alone.

### 5.1.3 Mass and Energy Balance Closure

The overall mass balance closures for the OPs listed in Table 2 do not deviate by more than 7%. There do not appear to be any systematic variations in response to changes in feedstock composition, reactor temperature or pressure. The deviation in carbon balance did not exceed 6%. The deviation in the energy balance closures is consistently in the range of 4-6% for both experimental runs. The relatively good closures of the overall mass, energy and carbon balances from experimental runs nearly a year apart indicate the relatively stability of the process and instill confidence in the general accuracy of the measurement equipment.

Compared to carbon balance, sulfur balance shows greater variation between experimental runs. The OPs in the experimental run presented in Paper I yield excellent closures with a maximum deviation of 4%. In contrast, the OPs from the experimental run in Paper II have a maximum deviation of 19% and a standard deviation of 7.4%. For sulfur, as well as for potassium and sodium the error in balance closures is likely linked to systematic errors in the measurement of GL element compositions, which have a measurement uncertainty of 10%.

## 5.2 Thermodynamic Equilibrium Calculations of Black Liquor Gasification

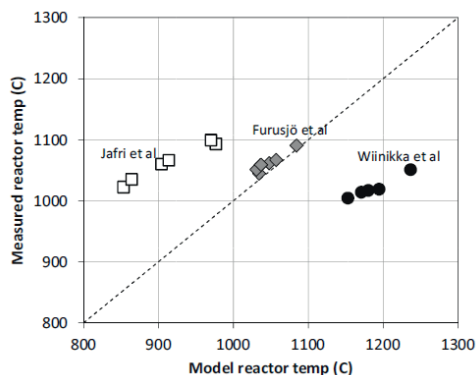
This subchapter uses selected results from Paper III to examine whether TECs can be used to predict BLG performance to a high degree of accuracy, as postulated in research question 3. TEC predictions of reactor temperature and gasification product compositions are validated using three experimental datasets. In order to understand the source of potential deviations between measured and predicted results, the sensitivity of the TEC model to variations in process inputs is also investigated.

### 5.2.1 Validation of Predicted Results with Experimental Data

A comparison between measured and predicted reactor temperature is shown in Figure 10. Temperature measurements are taken from pilot studies by Jafri et al. (Paper I), Furusjö et al., and Wiinikka et al., which are summarized in Chapter 4.2.1.

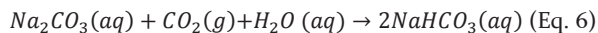
The predicted and measured temperatures show excellent agreement for OPs in the Furusjö et al., study. The agreement is significantly poorer for the two kraft BL-based studies (Jafri et al. and Wiinikka et al.). The deviation from measured temperatures is of the opposite sign in each case, which suggests that the root cause is specific to the study rather than to the feedstock type. The discrepancy between measured and predicted data is significantly greater than the span of temperature variation between OPs in the experimental data but lower than that contributed by the uncertainty in BL composition, as discussed in the next subchapter. It can also be noted that temperature variations within each data set agree well between experiments and equilibrium calculations.

The predicted flows of syngas species are compared with experimental measurements in Figure 11a. The predicted results for major syngas species agree reasonably well with experimental measurements. Quite expectedly, the agreement is not as good for minor species. Close to zero methane is predicted for the Furuşjö et al. and Jafri et al. datasets, whereas experimental data shows that 0.2-1.5% of the feedstock carbon ends up in methane. For the Wiinikka et al. dataset, there is better agreement as the predicted flows of methane are larger. However, since there exists an inverse correlation between methane concentration and reactor temperature, this may be due to the very low predicted temperatures that are significantly different from their experimentally measured counterparts.



**Figure 10. A comparison between TEC temperature predictions and reactor temperature measurements from Paper I, Wiinikka et al., [88] and Furuşjö et al., [69].**

Among the inorganic components, it can be seen from Figure 11b that for GL TIC, the experimental values consistently exceed the predicted amounts. Recall that TIC includes the carbon found in hydrogen carbonate and that hydrogen carbonate is present in GL but not in smelt at reactor exit. Assuming that the formation of hydrogen carbonate follows the route shown in eq. 6, its concentration can be used to calculate the amount of carbon dioxide absorbed in GL. The amount absorbed is, however, small relative to flow of carbon dioxide in syngas.



Predictions of GL sulfur agree fairly well with experimental data (see Figure 11b) for the Furuşjö et al. and Jafri et al. datasets. Since GL compositions are not provided in Wiinikka et al., a direct comparison with TEC predictions cannot be made. Figure 11a shows clearly that the flows of H<sub>2</sub>S, which is the pre-dominant sulfur-bearing component in syngas are over-predicted for two out of the three datasets. The exception is the Jafri et al. dataset but as explained in Section 3.3.2 of Paper III, the good agreement in this case is incidental and a consequence of the erroneously high predicted reactor temperature. Furthermore, the explanation for the good GL sulfur agreement in



the case of Furusjö et al. may lie in the fact that the reported sulfur balances do not close well, which suggests that the sulfur split is uncertain. The predicted flows of COS are larger than the measured values for all three datasets. This is likely down to the fact that COS does not reach equilibrium in the reactor and that some of the COS is hydrolyzed to  $\text{H}_2\text{S}$  during syngas cooling. Overall, it can be concluded that TEC should not be used to predict methane and distribution of sulfur species for BLG.

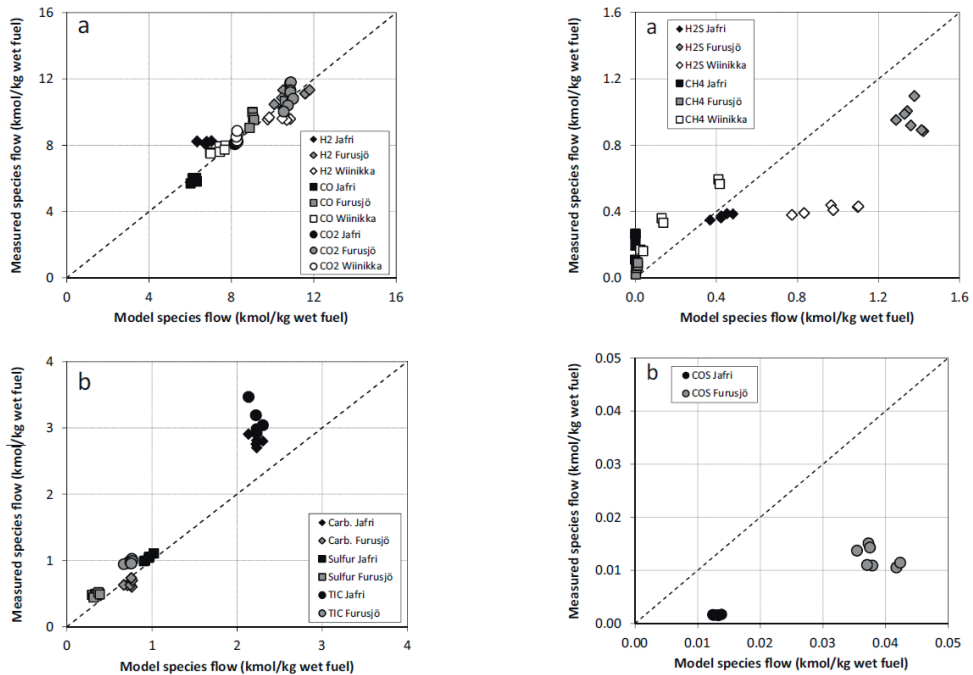


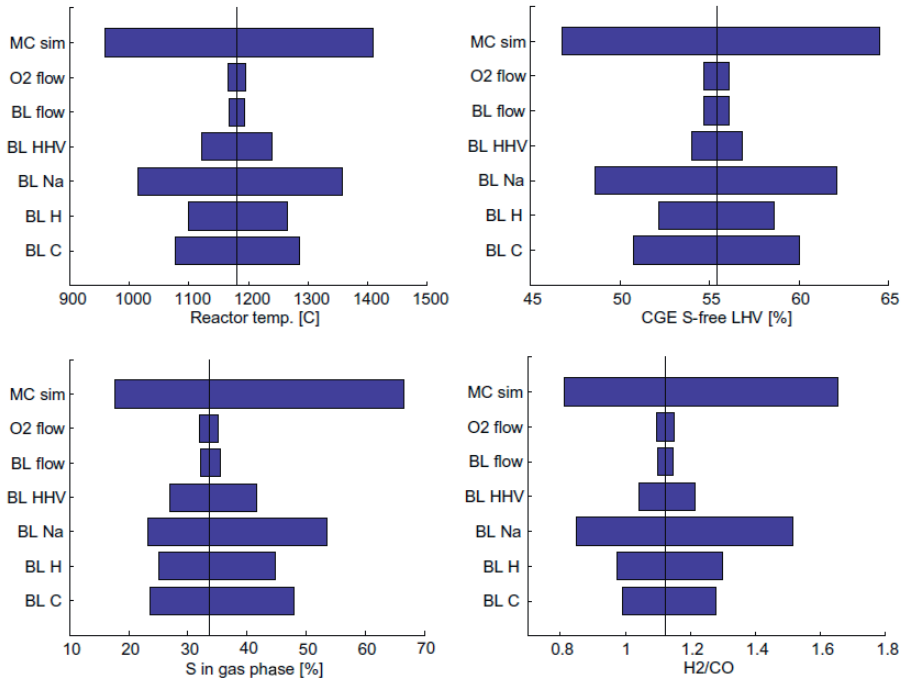
Figure 11. A comparison between measured and predicted results for major gas phase and liquid phase species for the datasets from Paper I, Wiinikka et al., [88] and Furusjö et al., [69].

### 5.2.2 Sensitivity to Variations in Input Data

It was shown in the previous subchapter that TEC predictions can deviate significantly from experimental measurements. The observed difference can be attributed to three main sources, or combinations thereof, namely, real deviations from equilibrium, errors in experimental data, and erroneous inputs to the TEC models. To assess the extent to which the above may contribute to the deviations observed, the effect of varying selected inputs on some important gasification performance indicators is illustrated in Figure 12.

It is apparent that TEC predictions of gasification performance are affected considerably by uncertainties in feedstock composition, while the contribution of the uncertainty in feedstock flow

measurement is less significant. The uncertainties in sodium and carbon content contribute to variations of over 200 °C in the predicted reactor temperature. Such variations exceed the practical operating envelope of the pilot-scale gasifier, which has significant implications for the agreement between TEC predictions and experimental measurements. In addition, the uncertainty in inputs is further amplified in the model as can be seen by comparing the relative uncertainty ( $2s_{rel}$ ) of  $\pm 2.6\%$  in the carbon content of BL with the resulting relative uncertainty of  $\pm 9\%$  in CGE.

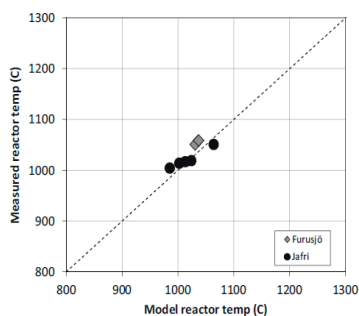


**Figure 12. Influence of uncertainty in TEC inputs on predictions of selected outputs for OP5 in Jafri et al. [141]. The vertical line is the predicted base case. Model inputs were varied one at a time within estimated 95% confidence limits with the exception of the bars labeled "MC sim" in which all BL constituents were varied simultaneously.**

The measurement techniques used for determining the composition of BL and STL are associated with relatively large uncertainties. It is assumed that the uncertainty values provided in the reference studies represent a coverage factor of two, i.e. an approximate confidence interval of 95%. On this basis, a pooled relative standard deviation was calculated for each element is tabulated in Table 2 of Paper III, which shows that most elements have a large uncertainty. The variation resulting from the combined uncertainty from all BL constituents is represented by MC sim in Figure 12 (see Section 3.1 of Paper III) and it has a greater impact on performance than the uncertainties from individual constituents or those from other studied inputs. It is worth noting that the uncertainty in fuel composition also creates an uncertainty in the stoichiometric oxygen

demand. The 95% interval for stoichiometric oxygen demand in the MC simulation is 0.75–0.86 kg O/kg BL, which suggests that the  $\lambda$  value can only be approximately defined from available experimental data.

Paper I notes a systematic deviation of 5–6% in the experimental carbon balance closure that is not present for the other investigated elements (Na, K, S). This also suggests that flow measurement errors may not be the main underlying cause and that feedstock uncertainty may be a contributory factor to observed deviations in predicted results. To test this hypothesis, the carbon content of the feedstock in the Paper I dataset was adjusted upwards until a full closure of the experimental carbon balance was achieved. This was done to eliminate, to the extent possible, the deviations caused by poor experimental data, thereby allowing the study of the real deviation from equilibrium.



**Figure 13.** The relationship between measured reactor temperatures and TEC predicted for selected/adjusted operating points with good carbon balance closure.

A comparison of the predicted reactor temperature for the adjusted Jafri et al. dataset and three OPs from the Furusjö et al. dataset that have a carbon balance closure deviation of less than  $\pm 2\%$  with experimental data is provided in Figure 13. It can be observed that changing the feedstock composition has a dramatic effect on the agreement between predictions and measurements, which is now excellent for all the OPs. It can be seen from Figure 7 in Paper III that the agreement for major gas species also undergoes an improvement. The average relative prediction error for hydrogen is reduced from 18% to 5% despite the fact that methane is not constrained. However, GL TIC still shows a disagreement between predictions and measurements, thereby indicating that the absorption of small amounts of  $\text{CO}_2$  in the GL is a real phenomenon. The difference in the case of the sulfur species also remains, indicating the presence of a real deviation from equilibrium.

The improved agreement discussed above does not prove that the error in feedstock analysis is the only source of error. It does, however, suggest it to be the most likely culprit and further emphasizes how uncertainties in feedstock composition can influence TEC predictions significantly. At the same time, the good overall agreement between predicted and experimental data when taking into

account known deviations from equilibrium shows that TECs represent a valuable tool for studying and predicting the gasification performance of spent pulping liquors.

An important thermodynamic assumption that strongly influences predicted results concerns the composition of the combustion products in the bomb calorimeter, which is used to estimate the feedstock enthalpy of formation. As discussed in greater detail in the Supplementary Material for Paper III the approach typically used for estimating the enthalpy of formation runs into problems when applied to high ash and high sulfur fuels such as BL or STL. A simplified approach is tested in which it is assumed that sodium and potassium form oxides (as opposed to carbonates and sulfates), sulfur forms sulfur dioxide (as opposed to sulfate) and carbon forms carbon dioxide (as opposed to a mix of carbonate and carbon dioxide). The simplified approach yields BL enthalpies of formation that are higher than those obtained using the conventional approach by 1.6 to 2.3 MJ/kg DS, which corresponds to ~10-20% of BL HHV. As expected, the resulting TEC predictions are very different, which highlights how critical it is to make correct assumptions about the composition of bomb calorimeter combustion products.

Given the extent to which the uncertainties in feedstock composition and assumptions about bomb combustion calorimetry products influence predicted results, it is hypothesized that the main contributor to the observed deviation between TEC predictions and experimental measurements is the error associated with the feedstock analysis. More information on how the hypothesis is tested and how other alternatives are precluded can be found in Section 3.3.3 of Paper III.

### **5.3 Techno-economic Evaluation of Biofuels from Kraft Black Liquor**

This subchapter addresses research questions 3 and 5 by presenting a synthesis of results from two studies (Papers IV/V and Paper VI) that evaluate the economic case for biofuels from BL using techno-economic models populated with best available experimental data. The economic evaluations are built on analyses of energy performance that take integration effects into consideration.

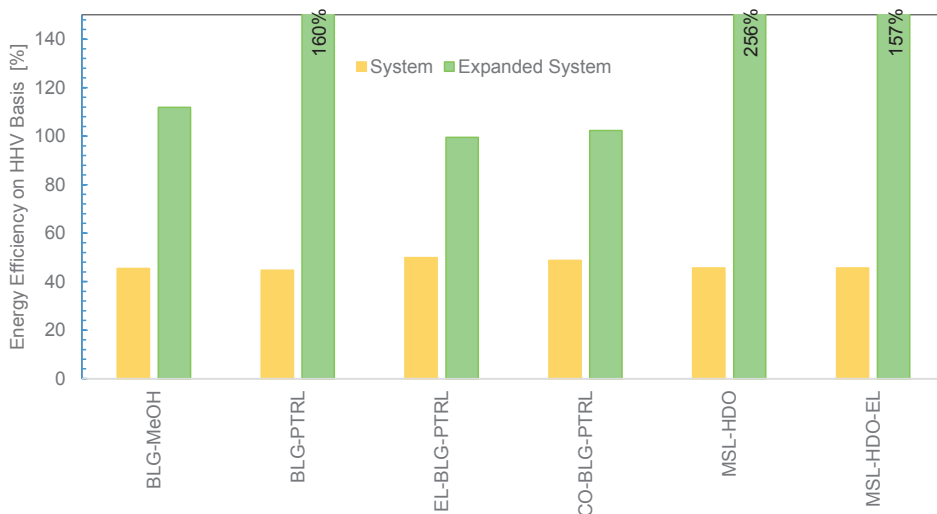
#### **5.3.1 Assessment of Energy Performance**

The energy performance of biofuel pathways integrated with the Model Mill is illustrated in Figure 14 using two different measures of energy efficiency. Results for the Södra and SKKP mills can be found in Section 4.3 of Paper VI. When calculating the system efficiency, only primary energy inputs are considered, while the expanded system efficiency also takes into account integration effects on mill and refinery energy balances (See Chapter 4.3.2).

System efficiencies are in the range 45-50%, which indicates that the energy performance of lignin-based and gasification-based pathways is relatively similar when evaluated on the basis of primary energy inputs. The high efficiency of the MTG process means that more than nine-tenths of the

energy in methanol ends up in the products. The bulk of the energy loss in the gasification pathways therefore happens during the gasification and the methanol synthesis steps, as well as, where applicable, during the production of hydrogen from electricity.

The marginal increase in system efficiency obtained by blending BL with 20 wt.% PO is quite close to that obtained by blending syngas with hydrogen. Note, however, that the loss of energy associated with the conversion of water to hydrogen is included within the system boundary, while the loss of energy during the conversion of biomass residue to PO is not included. System efficiencies in the lignin route are to a great extent determined by hydrogen consumption and product yields in the hydrotreatment step. It is worth recalling that, as discussed in Chapter 4.3.4, the hydrogen consumption and hydrocarbon yield structure for lignin hydrotreatment is based on experimental data of uncertain quality.



**Figure 14.** Energy efficiencies of biofuel pathways for the Model Mill case. See Chapter 4.3.2 for definitions of system and expanded system. Results for BLG-MeOH are from Paper IV and for all others from Paper VI.

Expanded system efficiencies are in the range 99-256%. The highest efficiencies are returned by MSL-HDO and BLG-PTRL. The results indicate that gasification-based pathways can offer an efficient route to biofuel production when the size of the biofuel unit is small in relation to the available energy surplus, which is the case for BLG-PTRL. On the other hand, BLG-MeOH is examined under the assumption that the gasification unit is replacing the RB at the mill (see Paper IV). Hence, additional biomass needs to be imported to satisfy the steam demand of the mill, thereby resulting in a lower efficiency. The expanded system efficiency of BLG-MeOH would be significantly higher if it were examined under the same assumption as that used for BLG-PTRL.

The heat demand of MSL-HDO is relatively high in the mill-integrated part of the value chain due to lignin purification requirements and increased evaporator load. However, as the biofuel unit is small relative to the size of the energy surplus at the Model Mill in Paper VI, the increased demand for steam is accommodated by reducing electricity exports to the grid. The lignin-based pathways, and to a lesser extent, the BL-based pathways also benefit from the assumption that energy gases and the heat released during hydrotreatment of lignin and upgrading of methanol can substitute for fossil-derived energy at the refinery.

Mills that have a negative energy balance (SKKP) or that are self-sufficient but do not operate a surplus (Södra) are, from an overall energy perspective, poorer candidates for the integration of biofuel production, as can be seen from a comparison of their performance with that of the Model Mill in Section 4.3 of Paper VI.

### 5.3.2 Profitability Comparison of Black Liquor-based Biofuel Pathways

The profitabilities of MSL-HDO and BLG-MeOH in a 2018 energy market scenario can be assessed from Figure 15 by comparing the respective *specific investment margins* and *annualized specific investment costs* of FOAK and NOAK plants. *Specific investment margins* and *annualized specific investment costs* for four forest residue-based pathways are also provided as a point-of-reference. Background information on the forest residue-based pathways can be found in Section 2 of Paper IV and Section 2.3 of Paper V. In-depth results are available in Section 3.2 of Paper V.

The profitabilities of FOAK MSL-HDO and NOAK BLG-MeOH investments compare favorably with FOAK and NOAK investments in forest residue-based pathways. It can be seen that relatively small BLG-MeOH units would appear under NOAK assumptions, even if the costs were to scale down less steeply than is assumed in this analysis. This represents an opportunity for pulp mills to debottleneck their existing RBs by using the surplus BL to produce biofuels for the transport market (as investigated in Paper VI). The breakeven size for a FOAK MSL-HDO plant comes out at ~30 MW, translating into a relatively modest required minimum investment of ~10 MEUR (Figure 11 in Paper V). Note that these numbers are meant to be indicative and given the large uncertainties in TCI estimates as well as the simplified scaling approach used in the analysis, they should be interpreted with caution. The availability of better data meant that process yields and investment costs for MSL-HDO were updated for Paper VI and a different economic evaluation approach was used, as discussed in Chapter 4.3.1.

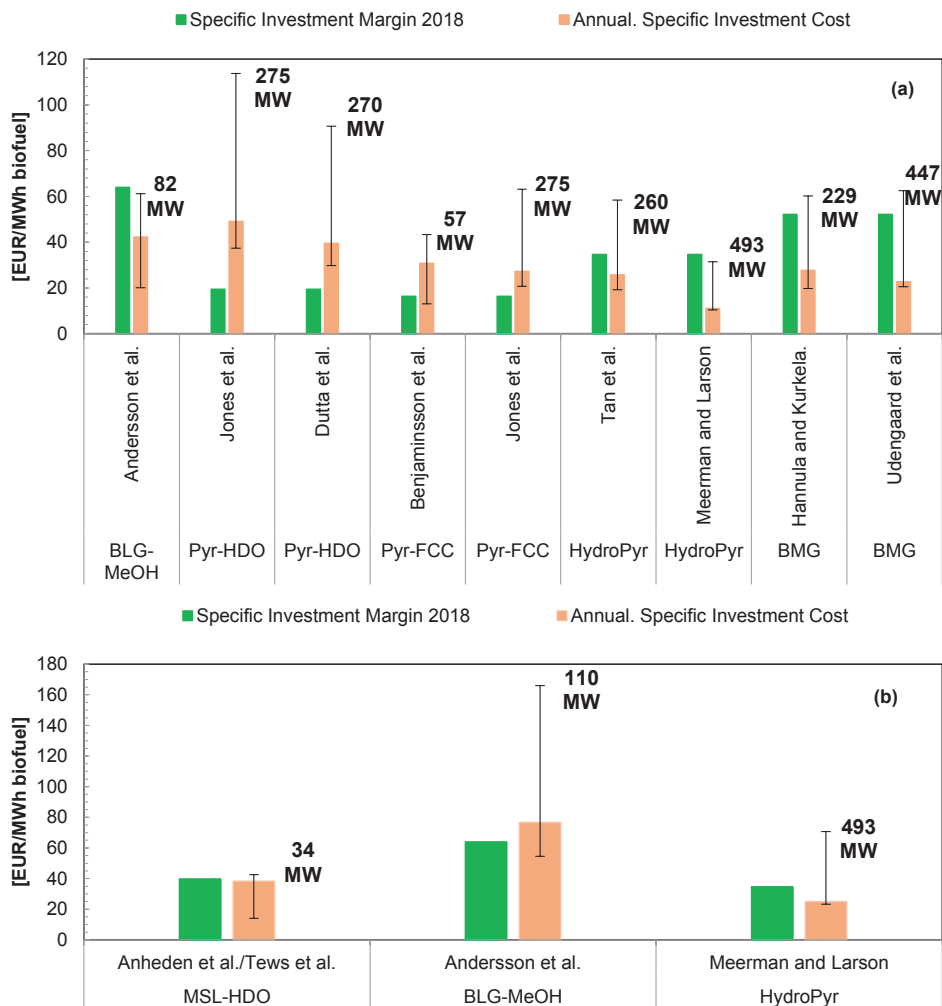


Figure 15. Specific investment margins and annualized specific investment costs for MSL-HDO and BLG-MeOH in relation to those for four forest-residue based pathways. A pathway is profitable when the specific investment margin exceeds the annual specific investment cost. (a) is based on nth-of-a-kind estimates and (b) on first-of-a-kind estimates. Boldface type denotes the biofuel production capacity specified in the source study and error bars show the effect of scale on annualized specific investment costs of plants in the range 25-600 MW. See Sections 2.3 and 3.2 in Paper V for more details.

### 5.3.3 Production Cost of Drop-In Biofuels from Black Liquor Part Streams

The cost of producing drop-in biofuels from BL part-streams using lignin and gasification-based pathways is illustrated in Figure 16 for each of the three mill configurations described in Chapter

3.2. The figure presents an itemized breakdown of production costs, which is used to calculate a MFSP for each pathway, as discussed in Chapter 4.3.1.

MFSPs for the Model Mill are consistently the lowest, varying between 77 EUR/MWh for BLG-PTRL and 133 EUR/MW for MSL-HDO-EL. MFSPs for Södra lie between 91 EUR/MWh for MSL-HDO and 147 EUR/MWh for MSL-HDO-EL. Biofuel production for SKKP is more expensive with MFSPs ranging from 104 EUR/MWh for BLG-PTRL and MSL-HDO and 152 EUR/MWh for MSL-HDO-EL. The results presented above indicate that integrating biofuel production with a pulp mill that operates with a large energy surplus (see Chapter 5.3.1) in relation to the size of the biofuel unit offers a significant economic advantage.

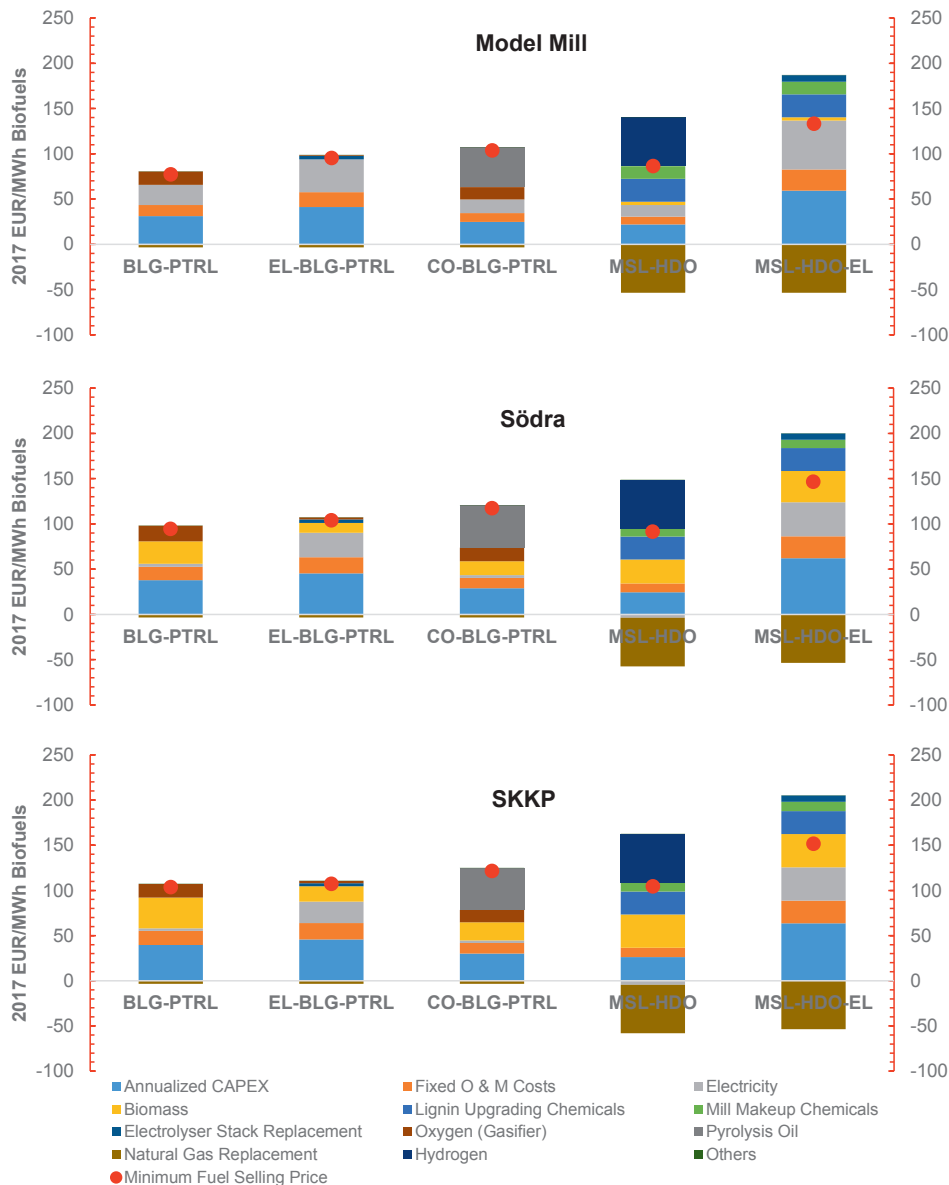
The prices of the lowest cost lignin and gasification pathways for the most advantageous mill configuration are better than or comparable to the reported economic performance of drop-in biofuels from other forest-based feedstocks [142]. A comparison of the lowest cost options also shows that both separation-hydrotreatment and gasification-catalytic synthesis can be used to produce drop-in biofuels from BL part streams at comparable cost.

The MFSP of MSL-HDO-EL is the highest amongst the examined pathways in all three mill configurations. A significant part of the total cost is attributable to the use of an expensive electrolyzer for hydrogen production. The economic case is likely to improve somewhat in the medium term if the projected decreases in the cost of electrolysis materialize. It nonetheless appears unlikely that MSL-HDO-EL will be able to compete with MSL-HDO on cost alone. However, the two lignin pathways swap rankings in an examination of GHG performance, as described in Chapter 5.4.2. Hence, an overall assessment of their performance across the aspects identified in Chapter 4.4 helps deliver a more complete picture of their relative merits.

A comparison of the gasification pathways shows that the gasification of unblended BL (BLG-PTRL) represents the least cost option for producing drop-in biofuels from BL part-streams. CO-BLG-PTRL has a higher MFSP than BLG-PTRL with the difference between the two amounting to 18-25 EUR/MWh. The economic performance of CO-BLG-PTRL is greatly influenced by the price of PO, which is taken to be 76 EUR/MWh in this work. A significant reduction in the price of PO is required to make the economic case for CO-BLG-PTRL comparable to that of better performing alternatives such as MSL-HDO and BLG-PTRL.

The MFSPs for EL-BLG-PTRL and BLG-PTRL differ by 4-18 MWh/EUR. The economic performance of the electrolysis-reliant EL-BLG-PTRL is sensitive to electricity prices (31-33 EUR/MWh, see Table 8 in Chapter 4.3.3) and PEM electrolyzer CAPEX (installed cost of 1500 EUR/kW). Future reduction in PEM electrolyzer CAPEX by a half would make the economic performance of EL-BLG-PTRL comparable to that of BLG-PTRL.





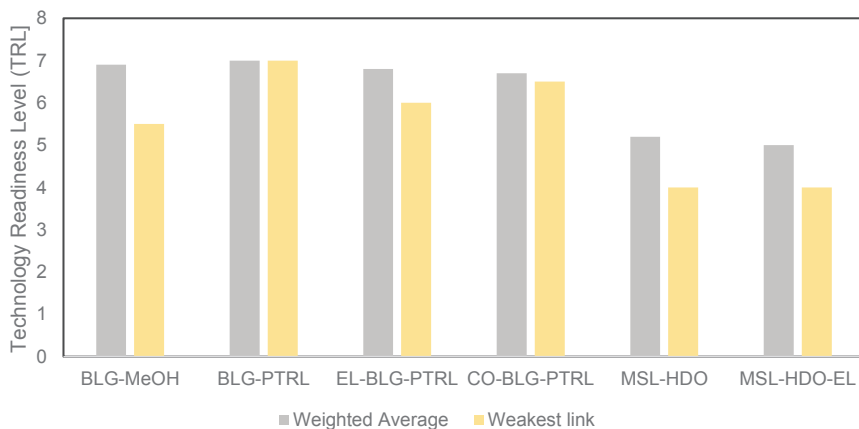
**Figure 16. Breakdown of biofuel production costs for black liquor-based pathways integrated with all three examined mill configurations.** “Lignin upgrading chemicals” are carbon dioxide, sulfuric acid and stabilization additive. “Mill makeup” covers additional sodium hydroxide and ESP ash disposal costs. The savings from the replacement from natural gas with energy gases are included as a negative cost. Costs associated with methanol synthesis catalyst renewable, zinc oxide replacement and fossil production are aggregated under “Others”.

## 5.4 Other Relevant Aspects

This subchapter responds to research question 4 with an examination of three aspects that influence economic viability and commercial deployment of biofuel technologies: (i) Technology maturity, (ii) GHG performance, and (iii) Biofuel production potential. The results presented here are taken from Papers V (aspects i, ii, iii) and VI (aspects i, ii).

### 5.4.1 Technology Maturity

Results from TRL assessments of examined BL-based pathways are compiled in Figure 17. The two complementary approaches used to determine TRL scores (the “weighted average” and “weakest link” approaches) are described in Chapter 4.4.1. TRL scores and assigned weights for BLG-MeOH can be found in Appendix B of the Supplementary Material for Paper V and those for the remaining pathways are provided in Section F1 of the Supplementary Material for Paper VI.



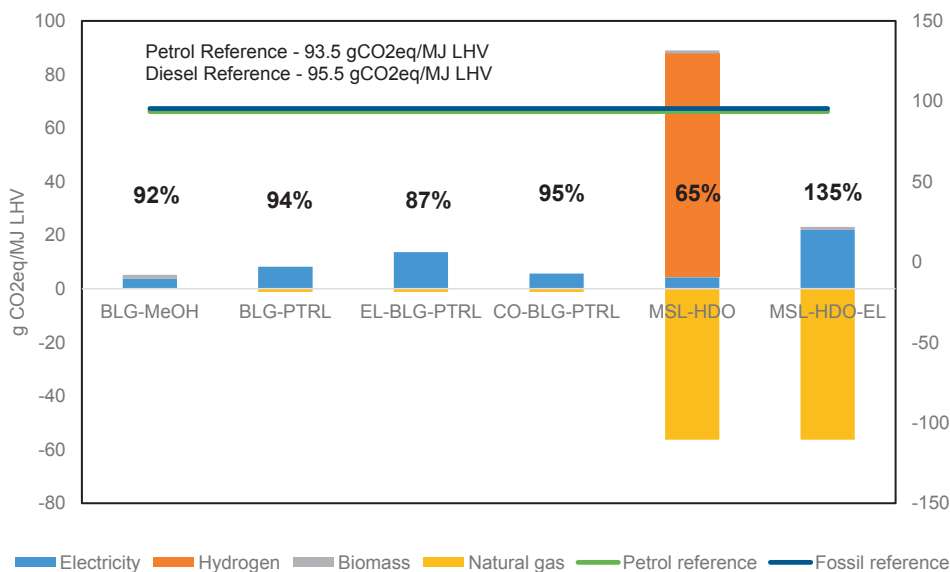
**Figure 17. Technology readiness levels for black liquor-based biofuel pathways.**

The results show that the gasification pathways score higher than lignin pathways under both of the studied approaches. The important individual process steps in the gasification pathways have all been demonstrated in pilot scale experiments leading to weighted average TRL scores ~7 [64], [113], [143]. The weakest individual steps (TRL 4) are the upgrading of GL to white liquor as a part of the full integration of the gasification unit with the pulp mill and the refinery integration of MTG, which has not been demonstrated but is considered fairly straight-forward and non-complex. The gasification unit in BLG-PTRL is intended as a complement to the RB, while the gasification unit in BLG-MeOH is designed as a RB replacement. The resulting difference in scale-up and integration complexity is the reason why BLG-MeOH scores lower than BLG-PTRL on the weakest link metric.

TRL scores for the most important individual steps in the lignin pathways are between 4 and 6, resulting in a weighted average score of 5.2 for both MSL-HDO and MSL-HDO-EL. The weakest links are the formation of a pure and stable intermediate lignin/VGO mixture from the separated lignin and the deoxygenation and cracking of this intermediate mixture. These steps have been assigned a score of 4, which corresponds to validation in lab-scale experiments. Note, however, that work is currently in progress to validate both these steps in pilot-scale experiments.

#### 5.4.2 GHG Performance

GHG footprints for black liquor-based pathways are shown together with those for selected forest residue-based alternatives in Figure 18. The emission calculations use a simplified approach derived from RED guidelines for emissions allocation (see Chapter 4.4.2 for more details). Compared to fossil-based petrol and diesel references of 93.5 and 95.5 gCO<sub>2</sub>eq/MJ, the studied biomass-based biofuels can deliver savings between 65% (MSL-HDO) and 135% (MSL-HDO-EL). All the gasification-based pathways meet the saving requirements set out in RED II as both the biomass and the electricity used as feedstock have low GHG footprints.



**Figure 18. GHG footprints of black liquor-based biofuel pathways. Estimated using RED methodology. Percentages in bold denote savings compared to fossil-based petrol and diesel references.**

The use of renewable electrolysis hydrogen in conjunction with the replacement of natural gas with fuel gases released during lignin hydrotreatment means that MSL-HDO-EL has a negative GHG footprint. With a reduction of 65%, MSL-HDO just about fulfills the stipulation of 65% GHG savings

for new-built plants in the RED II proposal. The same amounts of energy gases replace natural gas in both pathways but the use of fossil hydrogen in MSL-HDO cancels out the associated savings. The results for the two lignin pathways clearly show the advantage of using electrolysis hydrogen, under the assumption of a Swedish electricity mix, from a GHG accounting perspective.

The hydrotreatment of lignin also releases significant quantities of heat, which can be used to substitute for natural gas at the crude oil refinery. However, RED does not permit the allocation of CO<sub>2</sub> savings to a heat stream. Figure 13 in Paper V and Figure 9 in Paper VI shows that both MSL-HDO and Pyr-HDO would be able to meet RED II stipulations if emissions are allocated using the principle of system expansion.

### 5.4.3 Biofuel Production Potentials

Estimates for the Swedish biofuel production potentials of BLG-MeOH and MSL-HDO are given in Figure 14 of Paper V. In recognition of the large uncertainties inherent in ascertaining feedstock potentials, estimates are provided in the form of a range with a lower and an upper limit. BLG-MeOH and MSL-HDO have production potentials of 12 TWh/y to 27 TWh/y and 4 TWh/y to 10 TWh/y, respectively. These numbers correspond to ~13-29% and ~5-11% of the Swedish domestic transport fuel demand in 2017.

A key requirement for lignin-based pathways relates to the preservation of RB functionality, which means that technical extraction potentials represents a decisive limitation. The upper estimate for MSL-HDO assumes that 30% of all lignin in the Swedish kraft BL stock can be extracted. The lower estimate is obtained by reviewing mills individually and prioritizing the prevention of negative effects on mill operation. The resulting estimate of ~4 TWh/y is probably more realistic. Gasification-based alternatives have a higher upper limit than lignin extraction-based pathways. However, the transition from RB technology to the commercially unproven BL technology represents a key limitation. The lower limit for BLG-MEOH assumes that only pulp mills with boilers that need replacement due to old age would consider moving over to gasification. The resulting potential of ~12 TWh/y likely represents a more realistic ceiling for this route, at least in the short-to-medium term. The estimates for MSL-HDO do not take into account technical restrictions pertaining to co-feeding and co-processing at the refinery, which are likely to be site specific.



## 6 Concluding Remarks

*The research questions posed in Chapter 2 are answered below. A number of general conclusions and reflections based on the research findings are also presented. The chapter closes with a number of suggestion for further research.*

### 6.1 Answers to Research Questions

**Question 1:** *How is gasification performance influenced by blending black liquor with up to 20% pyrolysis oil by weight? (Papers I & II)*

Blending BL with up to 20 wt.% PO results in a notable overall improvement in syngas quality. The most significant effect is on the concentrations of CO and H<sub>2</sub>, which increase with increasing blend ratio, leading to a corresponding increase in the energy efficiency of feedstock conversion. Concentrations of minor (H<sub>2</sub>S and CH<sub>4</sub>) and trace (C<sub>6</sub>H<sub>6</sub> and COS) components are not greatly impacted. Like syngas from unblended BL, syngas from examined PO/BL blends is also virtually free of tars.

Analysis of TOC and sludge in GL samples shows that the carbon conversion efficiencies of unblended BL and PO/BL blends are comparable. This indicates that the catalytic effect of alkali in BL is not degraded by the addition of up to 20 wt.% PO, thereby corroborating earlier findings from laboratory studies in the literature. Recovering sulfur in reduced forms is important for successful integration with the kraft recovery cycle. Measurements of total sulfur and sulfide ions in GL are subject to large uncertainties, which are carried forward to the estimation of sulfur reduction efficiency.

**Question 2:** *Can thermodynamic equilibrium calculations of entrained-flow black liquor gasification predict product compositions and gasification performance to a high degree of accuracy? (Paper III)*

TECs are able to predict the composition of major syngas components (CO, CO<sub>2</sub>, H<sub>2</sub>) and slag products from BLG with high accuracy, particular when known deviations are taken into account. Since CH<sub>4</sub> is known to deviate from equilibrium, constraining it to experimentally measured values in the model generally improves the prediction of other gas components. The sulfur split between syngas and smelt that does not fully follow equilibrium is predicted less well. Better predictions require the implementation of empirical modifications to the model. Analysis shows that small errors in feedstock composition can have a relatively large influence on TEC predictions for some performance parameters. These errors likely have their origin in analytical uncertainty.

**Question 3:** *What does an evaluation based on best available experimental data reveal about the economic viability of producing biofuels from black liquor? (Papers IV, V and VI)*

The production of methanol from BL in n<sup>th</sup>-of-a-kind entrained-flow gasification plants intended as substitutes for RBs appears to be profitable in a 2018 energy market scenario for units as small as 50 MW<sub>th</sub>. The findings of the profitability analysis should be interpreted with caution as the scaling approach used is simplistic and the underlying investment estimate in the literature includes an investment credit for an end-of-life RB replacement. The production of drop-in diesel and petrol from BL via lignin separation in relatively small-scale units and subsequent hydrotreatment at a crude oil refinery also comes out as economically viable in the profitability analysis. Confidence in the results of the profitability analysis for this route, however, is on the lower side as the analysis is built on uncertain product yields and early stage investment data.

In the case of the production of drop-in biofuels from part-streams of BL, the best performing pathways yield MFSPs of ~80 EUR<sub>2017</sub>/MWh, which are comparable to or better than MFSPs from other forest-based alternatives. This indicates that drop-in biofuels from BL constitute an economically interesting option for meeting the rising demand for renewable drop-in fuels. The MFSP from the best performing lignin and gasification-based pathways are comparable, which indicates that neither of the two routes have a decisive economic advantage over the other.

A comparison of MFSPs for different mill configurations shows clearly that a mill operating with an energy surplus in the form of electricity represents the lowest cost option for integrating biofuel productions. Other mills have to import biomass to satisfy the energy demands of the biofuel production unit in both of the examined routes, which represents a significant cost. The economic case for each pathway is also subject to the influence of site specific capacity constraints on mill equipment, such as the power boiler, which can place limitations on acceptable biofuel plant size.

There are some notable differences in the expenditure and revenue structures of the different pathways, which could potentially lead to an alteration in economic viability if the energy market conditions were to change. This is particularly applicable to the gasification-electricity hybrid pathway (EL-BLG-PTRL), which is sensitive to electricity prices and electrolysis investment costs and the PO/BL co-gasification pathway (CO-BLG-PTRL), which is sensitive to the price of PO.

**Question 4:** *How do the most industrially relevant pathways for the production of biofuels from black liquor compare with each other in terms of technology maturity, greenhouse gas emissions and biofuel production potential? (Papers IV, V and VI)*

The gasification pathways have a somewhat higher level of technology maturity (TRL ~6-7) than the lignin pathways (TRL ~4-5) at the time of writing, which implies that they can potentially be deployed commercially at shorter notice. However, several important steps in the lignin track such as lignin separation and hydrotreatment are in the process of being demonstrated in industrially

relevant scale. Others are expected to follow suit in the near future given the heightened commercial interest in the route.

The feedstocks in the gasification pathways, namely biomass and electricity under the assumption of a Swedish electricity mix, have relatively small footprints. Hence, all of the studied gasification pathways are able to deliver GHG savings of 85-95%, thereby easily exceeding the stipulated 65% reduction for new-built plants in RED II. Based on available evidence, both lignin-based pathways can meet the RED II reduction target, but electrolysis hydrogen (MSL-HDO-EL) has a significantly smaller GHG footprint than fossil hydrogen (MSL-HDO).

The assessment of Swedish biofuel production potentials shows that while none of the pathways are able to meet the national demand for transport fuels on their own, both BL-based routes can make a significant contribution to the envisioned low-carbon transition. The upper limit for lignin pathways is determined by technical restrictions on the amounts that can be extracted without adversely affecting RB operation. The ceiling is theoretically higher for gasification pathways but the potential that can be realized realistically is dependent on the need and willingness of the mills to replace RBs with gasifiers.

**Question 5:** *How do gasification-based pathways perform economically when used to produce biofuels from part streams of BL and how is economic performance influenced by the use of pyrolysis oil and electrolyzer hydrogen as secondary feedstocks? (Paper VI)*

With a MFSP of ~80 EUR<sub>2017</sub>/MWh in the most advantageous mill integration scenario, the gasification of unblended BL comes out as the lowest cost option for producing drop-in biofuels from BL part-streams. While blending BL with PO or adding electrolysis hydrogen to syngas from unblended BL offer increased biofuel production potentials and improved feedstock diversity, these benefits are not accompanied by better economic performance. Co-gasification of BL and up to 20 wt.% PO could become economically competitive if the price of PO were to fall by a third. Adding electrolysis hydrogen to syngas from unblended BL could also be economically competitive if the investment cost of PEM electrolysis were to fall by a half.

## 6.2 General Conclusions and Reflections

Blending kraft BL with fast PO was shown to improve biofuel yields without compromising GL quality, which is important for successful integration with a pulp mill. This indicates that feedstock diversification represents a technically viable option for increasing the biofuel production potential of BL. At the same time, the gasification of unblended BL offers the best route for converting the electricity surplus at the pulp mill into biofuels from a cost perspective. The price of PO is high, which means that the economic performance of PO/BL blends is worse than that of unblended BL when assessing production in small gasification units intended to debottleneck capacity-constrained RBs. The use of PO for the manufacture of transport fuels also has implications for



general biomass use, especially in light of future competition from industrial sectors that may also rely on sustainable biomass-based residues for de-fossilization.

The economic case for biofuels from BL was found to be influenced considerably by the energy profile of a given mill, which therefore needs to be considered explicitly in economic evaluations. Mills that have no or a small surplus in the form of electricity must import biomass, provided enough capacity exists in their power boilers in the first place, especially if syngas is supplemented with electrolysis hydrogen. This indicates that resource and energy efficient market pulp mills may make the best candidates for co-location and integration of lignin and gasification-based biofuel production units. The fraction of BL that can economically be used for biofuel production is determined by mill-specific considerations such as technical limitations on lignin extraction and spare capacity in existing units.

The comparatively high TRL of the gasification pathways implies a shorter lead time to commercial deployment. Owing to the absence of feedstock other than biomass and electricity and the assumption of a Swedish electricity mix, the GHG performance significantly exceeds minimum requirements. Even though the efficiency of the initial conversion step to an intermediate product is relatively low, the conversion of the intermediate product to petrol blendstock can be achieved with high efficiency. These attributes make the BL gasification track a reasonable contender for the production of renewable petrol in the context of the Swedish biofuel market, which is currently faced with a shortage of suitable alternatives to fossil petrol.

In the lignin separation-hydrotreatment route, the use of fossil hydrogen for lignin hydrotreatment offers significantly superior economic performance, while the use of electrolysis hydrogen for the same purpose returns significantly greater GHG emissions. It appears unlikely that the electrolysis-based alternative will be able to compete on economic grounds in the near future unless there is a sharp decline in investment costs for PEM electrolyzers that coincides with a steep rise in natural gas price. The TRL of the hydrotreatment step is currently low, and the resulting absence of good quality experimental data means that the economic and GHG performance of the lignin separation-hydrotreatment route is subject to some uncertainty. Based on current evidence, the lignin route appears better suited to the production of drop-in diesel blends as petrol yields are miniscule.

Since the demand for forest-based drop-in alternatives that can replace both petrol and diesel is expected to grow in the face of a sustained legislative push, the complementary deployment of gasification-catalytic synthesis and lignin separation-hydrotreatment can be a strategically interesting option for achieving deep reductions in transport GHG emissions.

### **6.3 Further Work**

The discussion of further opportunities for research based on the findings presented in this work is divided into two parts.

### 6.3.1 Black Liquor Gasification Development

Any sulfur that is not present in GL in reduced form does not play an active role in chemical cooking and thereby has a negative impact on mill operation. The methods used for estimating the concentrations of sulfide ions and total sulfur in GL have relatively large uncertainties, which makes an accurate quantification of sulfur reduction efficiency highly challenging. In addition, GL from the pilot experiments was exposed to the atmosphere during initial sampling and further oxidation may have taken place while samples were being prepared for analysis. In conjunction with analytical limitations such as the absence of a suitable method for quantifying elemental sulfur, this meant that identification and characterization of the sulfur species present in GL under typical operating conditions was not possible. Further research on the study of sulfur chemistry in gasification GL and on method development for characterizing the sulfur species present therein is therefore suggested.

The performance of BLG is sensitive to naturally occurring variations in BL composition, which originate in the mill. This thesis does not present a systematic analysis of the effect of long-term variations in BL composition on process performance. Observations from different experimental runs indicate that these variations have a noticeable influence on important performance parameters such as CGE. The study of expected fluctuations in process performance is potentially of significant relevance in relation to effects on operation and economic forecasting if the process is scaled up. An assessment of long-term natural variations in gasification performance is thus advised as a de-risking step before commercialization.

The technical viability of gasification PO/BL blends has been demonstrated for blends with up to 20 wt.% PO and the resulting increase in biofuel yields and, consequently, production potentials from a fixed amount of BL has been documented. Laboratory-scale investigations of PO/BL blends in the literature indicate that blends with higher PO fractions can be gasified provided the beneficial catalytic effect of alkali is maintained, which can be achieved through the addition of sodium hydroxide. The study and demonstration of PO/BL blends with PO fractions in excess of 20 wt.% in pilot experiments therefore represents a natural continuation of co-gasification experiments. At the same time, it has been shown that the economic case for blending BL with PO is not very favorable, primarily on account of high PO costs. It may therefore be interesting to look at other cheap, plentiful and RED II-compliant forest-based feedstock such as bark that can be co-gasified with BL through the use of a suitable intermediate step such as hydrothermal liquefaction. Hence, the study of such a concept in pilot-scale experiments is suggested.

One of the pathways techno-economically examined in this thesis is the addition of electrolysis hydrogen to syngas from unblended BL (EL-BLG-PTRL). Although the major steps have all individually a relatively high level of technology maturity, the pathway in its entirety has not been demonstrated experimentally. It is advised that the addition of electrolysis hydrogen to syngas from

unblended BL is studied in pilot scale experiments to assess performance and demonstrate technical viability.

### **6.3.2 Modeling and Techno-Economic Evaluations of Biofuels Pathways**

It has been shown that TEC predictions of BLG are highly sensitive to errors in feedstock composition that have their origin in analytical certainty. While entrained-flow gasification generally follows thermodynamic equilibrium, it is suggested that TEC predictions are validated against experimental data, especially when assessing different feedstock mixes, to identify potential deviations and avoid misattribution of underlying causes.

The most significant data gaps in the lignin separation-hydrotreatment route relate to the hydrotreatment of lignin at the refinery. It is strongly recommended that hydrotreatment experiments of representative lignin and VGO co-feeds are carried out so that important characteristics such as hydrogen consumption and hydrocarbon yield structure can be established with greater confidence. The reduction of steam and additive consumption during lignin separation and purification can reduce operating costs significantly. An investigation into the possibility as a part of future development and optimization work is advised.

Given the high investment cost of PEM electrolysis, it is recommended that cheaper alternatives such as alkaline electrolysis are also looked at in future work on renewable hydrogen alternatives for lignin hydrotreatment.

One of the pathways that is not examined in this work, and which has of late received some attention for its relevance to the mitigation of GHG emissions from aviation is the FT synthesis of liquid biofuels from BLG syngas. FT synthesis is typically characterized by low product selectivity and the liquid hydrocarbon components requires further treatment before use. Recent advances in selective FT synthesis, which, however, is at a relatively low level of technology maturity, suggests that the pathway could potentially become more industrially relevant in the short-to-medium term, particularly for the production of jet fuels. A techno-economic evaluation of the possibility of producing jet fuels from BLG using refinery-integrated FT synthesis may therefore be merited.

The trade-off between some of the examined pathways in terms of cost, GHG footprints and technology maturity show that there is a clear case for the use of a more methodical multi-aspect assessment approach when evaluating and comparing emerging biofuel technologies. A general recommendation is that studies looking to evaluate biofuel pathways explicitly carry out an assessment of technology maturity in conjunction with economic and GHG performance assessments. In recognition of the importance of recycling biogenic carbon, another aspect that is of interest is the carbon utilization efficiency, which has not been examined in this work. An investigating of the challenges and possibilities linked to the improvement of carbon utilization in forest-based biofuel pathways is suggested as an interesting future research avenue.

## 7 References

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