Entrained-Flow Gasification of Black Liquor and Pyrolysis Oil

Pilot-Scale and Equilibrium Modelling Studies of Catalytic Co-gasification

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Energy Engineering
Licentiate Thesis

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Abstract

The last couple of decades have seen entrained-flow gasification of black liquor (BL) undergo an incremental process of technical development as an alternative to combustion in a recovery boiler. The ability of the technology to combine chemical recovery with the production of clean syngas renders it a promising candidate for the transformation of chemical pulp mills into integrated forest biorefineries. However, techno-economic assessments have shown that blending BL with the more easily transportable pyrolysis oil (PO) can not only increase the energy efficiency of the conversion process for methanol production, but also remove a significant roadblock to commercial deployment by partially decoupling production capacity from BL availability. The verification and study of catalytic co-gasification in an industrially relevant scale can yield results that are of both scientific interest and practical use for further technological development and eventual commercial deployment. Yet, it is a costly and time-consuming enterprise. Under certain circumstances, the expense and time involved may be reduced by performing thermodynamic equilibrium calculations (TECs) using a model that has been validated with relevant experimental data.

The main objective of this thesis was to study and quantify the gasification behaviour and process performance of BL and PO blends in pilot-scale. A secondary objective was to investigate catalytic entrained-flow gasification of biomass for a wide range of compositions using thermodynamic equilibrium calculations.

BL and PO blends were gasified at the LTU Green Fuels pilot plant in a series of experimental studies between June 2015 and April 2016. Of the 26 operating points for which mass balance calculations were performed, 25 returned closures of 100±5%. Compared with syngas from pure BL, the syngas from the blends was richer in CO and there were no signs of an increase in either soot or tar formation with increasing fractions of PO in fuel. Consequently, the cold gas efficiency went by up to 5%-units for the 20% PO blend. The carbon conversion efficiency was in the range 98.8-99.5% and did not vary systematically with either fuel composition or temperature. Unconverted carbon was almost exclusively present as dissolved organic carbon in the green liquor stream. Based on the results from the study, the gasification of blends with PO fractions greater than 20% was found to be practically feasible in a black liquor gasifier equipped with a PO/BL mixer and a PO feeding unit.

The results from the thermodynamic equilibrium calculations show that the highest cold gas efficiencies were returned by solid compositions with low O/C and H/C ratios, while the large H2/CO ratios were returned by fuel compositions with the higher fuel moisture content of 25%. The quantification of gasification performance using thermodynamic equilibrium in terms of the elemental ratios of feedstocks provides an efficient means of comparing fuels and estimating differences in potentially interesting parameters such as cold gas efficiency, external oxygen costs and shift loads between solid and liquid feeding.
List of Appended Papers

This licentiate thesis is based on the following papers

Paper I.

Paper II.

Paper III.
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1 Introduction
This chapter includes an overview of the push towards the development of biofuels and biorefineries in Sweden. It provides a short survey of gasification technologies and introduces the concept of catalytic co-gasification. It ends with a statement of the thesis objectives.

1.1 The Push towards the Development of Biofuels and Biorefineries
In the last few decades, Swedish energy policy has been driven by a desire to secure the supply of energy from renewable sources that are available domestically[1,2]. This focus was significantly bolstered by the European Union’s adoption of the 2020 renewable energy targets. Sweden’s head start in comparison to several other states in the union saw it meeting the target of 10% renewable fuels in the transportation sector by 2020 well in advance of the stipulated deadline[3]. Since then, energy goals have been designed, and adopted into legislation, to not only meet but exceed the requirements set down in the EU’s energy strategy for the period until 2030.

On top of the transport-specific energy goals[3] that have been adopted by the Swedish parliament, the reigning government has made clear its medium-term ambition of a national vehicle fleet that is fossil-fuel independent by 2030. In 2013, energy use in the transport sector amounted to 113 TWh[3]. The push towards fossil-fuel independence in the transport sector is part of a vision that would see Sweden go entirely fossil-free by 2050 and cut greenhouse emissions down to a nominal figure[2,3]. According to data compiled by the Swedish Energy Agency, the proportion of renewable energy in the national energy mix amounted to 52% in 2015 and was slated to increase further by 2020[3]. In contrast, the same report found that the proportion of renewable energy in the transport sector amounted to a meagre 15% in the same year. On a more global level, the development and widespread deployment of cost-competitive liquid biofuels has also been identified as key to success in the march towards the de-fossilisation of the transport sector by the European Union[4–6]. At the same time, it is an unavoidable fact that the use of biofuels is mired in controversy[7]. Yet, much of the polemic surrounding issues such as land-use change[8], and the whole food vs. fuel debate, can be avoided by focusing on the production of advanced biofuels from forestry residues and other wood-derived waste products[9]. It must, however, be noted that the above is generally only possible in localities where forestry residue that is usually classified as “waste” is easily and cheaply available in required amounts year round.

A recent forecast of Swedish energy scenarios in 2050 by the Swedish Environmental Research Institute found that unlike in several other states of Europe, it was not electricity that was limiting the expansion of renewables[2]. Instead, the major challenge to the realisation of the government’s lofty ambitions lay in the transportation sector, which required a large-scale transition from fossil fuels to renewables. The report further highlighted the need for the development of sufficient biofuel production capacity domestically. Given the importance of bio-based resources to Sweden’s economy,
this capacity can be developed in a resource efficient manner by converting existing biomass-based infrastructure such as pulp mills[10] and even combined heat and power plants[11] into biorefineries with poly-generation[12].

On the technological front, the gasification of lignocellulosic biomass feedstocks such as black liquor has long been suggested as a resource-efficient thermochemical process for the production of biofuels or biochemicals[13].

1.2 Gasification Principles and Technologies

Broadly, gasification may be defined as the partial combustion of carbonaceous material into gaseous products with a useable heating value. In most cases, the gas mixture is composed mainly of CO, CO₂, H₂, H₂O, CH₄ and tars such as benzene, naphthalene and toluene in varying amounts. However, depending on fuel composition and reaction conditions, other gases such as H₂S may also be present. The final composition of the mixture is generally determined by a combination of several factors not limited to: the composition of the fuel, the supply and nature of the oxidizing agent, pressure and the rate at which the material is heated. In slagging entrained-flow gasifiers, the slag is made up of ash and unconverted carbon in the form of char. H₂ and CO together are often referred to as synthesis gas, or syngas in short. They can be used together with small amounts of CO₂ as building blocks for the synthesis of a wide range of products such as methanol and subsequently dimethyl ether (DME), methane (usually referred to as substitute natural gas or SNG) through methanation and liquid hydrocarbons through the Fischer-Tropsch process.

Gasification made its first appearance on an industrial scale in the middle of the 19th century, when it was used to convert coal, and later oil, into town-gas for cooking and lighting. Afterwards, in the early decades of the 20th century, it was used to synthesise ammonia for the production of fertilizers. More recently, since the 1970s, the Sasol-Lurgi's fixed-bed dry bottom gasifiers in South Africa have produced syngas from sub-bituminous coal for Fischer-Tropsch synthesis. Entrained-flow variants developed by the likes of GE Energy, Shell, Siemens and ECUST in China continue to be used to convert different varieties of coal to syngas in the petrochemical industry[14].

Although several different types of gasifiers have been developed over the years, the designs can be grouped into three types: the fixed (or moving) bed gasifiers, the fluidised bed gasifiers and entrained-flow gasifiers[15]. These types can further be classified on the basis of whether they are updraft, downdraft or cross draft in the case of the fixed bed, or bubbling, circulating or dual in the case of fluidised beds[15]. Today, entrained-flow gasifiers and fluidised bed gasifiers are the two most common reactor types for production of syngas in large volume, although some moving bed gasifiers, which are similar[15] in form and function to their boiler equivalents, are also in operation. Recent trends in coal gasification projects show that the moving and fluidized-bed technologies are on their way out in favour of entrained-flow gasifiers[16].
Fluidised bed gasifiers work on the basis of the principle of fluidisation. The feedstock, which has been milled to an appropriate size enters the reactor from the side. Inside the reactor, it is suspended in a bed of either inert or catalytic particles by a gas that enters from the bottom at a suitably high velocity and acts as both the oxidising agent and the fluidising medium. Nearly all variants promote good mixing between the oxidant and the fuel, which facilitates both mass and heat transfer. Other features include comparatively long residence times and gas temperatures that range between 750°C and 1050°C. Since they tend to be non-slagging in nature, the “stickiness” point of the ash in the fuel generally sets the temperature ceiling. Due to the nature of the design and consequent operating limitations, some of the carbon remains unconverted and the raw syngas is characterized by significant quantities of tar and high methane content.

Entrained-flow gasifiers are categorised by pressurised operation in slagging mode at higher temperatures of between 1050°C for the anomalous case of black liquor to over 1500°C[14] for certain varieties of coal. The fuel and the oxidant are injected co-currently, typically in liquid form, through a nozzle into a refractory-lined or a cooled membrane-walled reactor. Gas residence time is in the order of a few seconds and the fuel particles typically undergo nearly complete conversion to a syngas rich in CO and H₂ and low in CH₄.

1.3 Developments in Biomass and Black Liquor Gasification

Even though entrained-flow gasification of solid biomass[17] underwent a period of growing interest and development in recent years, fluidised bed gasifiers are the more established and attractive option for the gasification of solid biomass because of their ability to handle solid feeding at atmospheric pressures. There was a spurt of growth in biomass gasification during the first decade of the 21st century that saw the inauguration of an 8 MWth dual fluidized bed gasifier in Güssing, Austria[18], albeit on the back of incremental development reaching back into the 1990s. The Kymijärvi II waste-to-gasification facility near Lahti, Finland, which was launched in 2012 recently went past more than twenty-five thousand hours of commercial operation[19]. In 2013, as the second stage of the bioliq® Project[20], a pressurized, entrained-flow gasifier was commissioned in Karlsruhe, Germany for the conversion of PO obtained from the liquefaction of lignocellulosic biomass. In the same year, the demonstration plant built by Haldor Topsøe A/S and project partners in Des Plaines, US first started producing gasoline from woody biomass using the pressurised, oxygen and steam blown fluidised bed gasification technology developed by Andritz Carbona[21]. More recently, the year 2015 saw the commissioning of the 20 MWth GoBiGas plant in Gothenburg, Sweden, which uses an indirect fluidised bed gasifier to convert woodchips and forestry residue into Bio-SNG[22].

Yet another strand of development has focused on the gasification of black liquor (BL) in entrained-flow gasifiers at low temperature. BL is a by-product of the kraft pulping process. In this capacity, it can be thought of as both a by-product of chemical pulping and a biomass-based feedstock in its own
right. The Kraft pulping process converts biomass-based feedstocks such as wood into high quality cellulosic pulp using a solution of sodium sulphide (Na₂S) and sodium hydroxide (NaOH) at a pH greater than 12 and a temperature around 170°C. BL is an alkaline mixture of the aforementioned pulping (cooking) chemicals, dissolved lignin and polysaccharides in roughly equal amounts on a mass basis. The exact composition can vary from mill to mill depending on factors such as the pulp yield, the composition of the cooking chemicals and the type of biomass used as feedstock. All Kraft black liquors are rich in alkali metals, mainly sodium, and have high moisture contents. Typically, at a modern pulp mill, black liquor is combusted in a special type of boiler called the recovery boiler to simultaneously generate process heat and electricity as well as recover the cooking chemicals for reuse. This closed cycle is also known as the recovery cycle.

First proposed in the 1960s as a recovery boiler alternative, black liquor gasification (BLG) is a niche process within a rather nascent field that has seen the primary drivers behind its development change greatly over time. In spite of its often-touted potential and the incremental development of competing variants in parallel over several decades, the technology has not succeeded in progressing beyond the fringes of commercialisation. The development history of BL gasification from its inception to the year 2008, which may be viewed in retrospect as the cusp of the latest cycle of development was summarised a few years ago by Whitty. In this paper, which was written in 2008, the author expressed the hope that due to the coming together of what they saw as the three key elements for successful commercialization, namely, a feasible, demonstrated technology, a strong market and (availability of) financial support, the next few years were likely to bring “the first integrated biorefineries incorporating black liquor gasification…” to our middle. Today, in a climate that is rife with considerable policy and environment uncertainty, this has not yet come into being. However, as recounted earlier in the chapter, several technical demonstration projects have been inaugurated recently and technological development continues to press on. Meanwhile, the pressurised oxygen-blown entrained-flow variant of BLG, which was originally developed by Chemrec AB on the back of several years of stepwise development, has evolved to form the basis of catalytic entrained-flow gasification. This concept relies on the use of metal catalysts such as alkali metals like sodium and potassium to achieve very high carbon conversion of both liquid and solid biomass-based feedstocks at low temperatures and short time-scales.

1.4 Catalytic Co-Gasification of Liquid Biomass

Black liquor can contain up to 20 wt.% of alkali in salts of sodium and potassium on a dry basis. The alkali metals in these salts have been shown to catalyse the gasification of char from BL, coal, solid biomass and BL/PO blends. The amount of alkali in fuel may be quantified in terms of the molar ratio of elemental alkali to carbon. This ratio needs to be sufficiently large to allow the realisation of the catalytic effect, which is dependent on the retention of a certain amount of alkali in the char. It is the existence of this catalytic effect, which permits high fuel throughput and
nearly complete carbon conversion at relatively low temperatures, that renders BLG a particularly attractive technology for biofuel production[33]. Even so, BL is a relatively energy-poor fuel compared to typical biomass-based counterparts. It is not transportable; the total volumes available are limited and inextricably tied to pulp production at a given location. Since the timely recovery of pulping chemicals is crucial to the functioning and economy of a pulp mill, very high availability factors, comparable to those of a recovery boiler, which is a mature technology, are required of potential commercial-scale installation, thereby promoting redundancy and pushing up capital costs. In face of these challenges, blending black liquor with the more easily transportable and energy-dense pyrolysis oil offers a means of unlocking and efficiently increasing the production potential of biofuels from BLG through the use of existing supply chains[34,35]. It has been shown that PO can be produced sustainably from biomass feedstocks such as a straw and forestry residues via e.g. a fast pyrolysis process[36].

A techno-economic evaluation of methanol production through black liquor and pyrolysis co-gasification showed that, in comparison with unblended BL, the gasification of a 25/75 PO/BL blend resulted in a doubling of methanol production and a 4%-points increase in energy efficiency[37]. In another study on large-scale implementation of PO/BL gasification for different pulp mill capacities, it was shown that gasification of 20-50% PO blends improved the economic case for small pulp mills in the range of 200-300 kATt/y, thus somewhat mitigating the advantages afforded by economies-of-scale[35].

The technical feasibility of BL/PO gasification was initially evaluated in a lab-scale thermo gravimetric analyser (TGA) and droplet conversion study, which investigated the influence of blend ratio on fuel conversion under gasification conditions[32]. The study found that, owing to the catalytic effect of the indigenous sodium, blends with up to 30% PO yielded fuel conversion times that were an order of magnitude below those needed for pure PO, and comparable to those for black liquor. In other words, char gasification, which is the rate-limiting step in the conversion process, did not appear to be adversely affected by the addition of pyrolysis oil. Recently, work has been initiated in the area of alkali-catalysed gasification of glycerol[26] and pine woodchips[38] and studies on the influence of alkali species in gas phase on tar cracking and soot reduction are currently on-going at Luleå University of Technology.

### 1.5 Aim of the Thesis Research

In the lead up to the present work, studies on BL/PO co-gasification had primarily focused on studying the effect of alkali on droplet and char conversion rates at low temperatures (≤900°C) and atmospheric pressure[32]. These conditions are different from those likely to be encountered in actual oxygen-blown pressurised entrained-flow gasifiers, namely, high (flame) temperature, high heating rates, and the resulting significant alkali release. Moreover, syngas compositions and process energy efficiencies
at different PO/BL blends ratios had only been estimated by simulation and, therefore, required validation, further study and detailed experimental quantification in a more industrially-representative scale.

Hence, the main aim of this thesis research was to study, understand, quantify and compare the gasification behaviour and process performance of BL and PO blends in pilot-scale.

To meet this aim, the specific objectives were to:

1. Determine experimentally concentrations of key process elements in all streams entering and exiting the gasifier for both pure black liquor [Paper I] and black liquor/pyrolysis oil blends [Paper II];
2. Quantify carbon conversion and cold gas efficiencies for different process conditions within the gasifier’s operational envelop by carrying out comprehensive mass and energy balances using measured data [Papers I and II];
3. Identify previously un-discovered process phenomena [Papers I and II]; and
4. Quantify the effect of blend ratio and reactor temperature on the process performance [Paper II].

A secondary aim of this thesis, which underlay the results presented in Paper III was to investigate the catalytic entrained-flow gasification of biomass for a wide range of elemental compositions using a thermodynamic equilibrium model validated against results of the co-gasification experiments.
2 Methods
This chapter summarises the black liquor and pyrolysis oil co-gasification experiments at LTU Green Fuels pilot plant, Piteå. It includes a comprehensive description of the gasifier and details of experimental procedure as well as the analytical instrumentation. It includes definitions of parameters used for fuel characterization and performance assessment and a description of the equilibrium model used in the thermodynamic equilibrium calculations.

2.1 Overview of Black Liquor and Co-Gasification Studies at LTU Green Fuels Pilot Plant
This work summarises key findings from several studies on the co-gasification of black liquor and pyrolysis oil that were carried out at LTU Green Fuels pilot plant in Piteå, Sweden between June 2015 and April 2016. Additionally, it also presents the results from a five-day long study on Kraft black liquor alone. This study was performed in September 2014 with the aim of thoroughly benchmarking the process in the lead-up to the co-gasification experiments. It represented the first systematic attempt at fully mapping and quantifying the performance of the gasifier at different operating points within its operating envelope. This study forms the basis of the first paper in this compilation; further details on experiment design and feed data can be found under “Experimental Conditions” in Paper I.

The first successful co-gasification of pyrolysis oil and black liquor took place on the 23rd of March, 2015 when a 7 wt.% PO blend was fed to the gasifier at 15 bar for four hours. Following the initial demonstration of the concept, the effect of blend ratio and reactor temperature on the gasification characteristics of the blends was systematically studied in a continuous, five-day long experimental run between the 31st of May and the 5th of June, 2015. During this time, the gasifier was alternatively operated on three PO/BL blends and pure black liquor at eight distinct settings. The study design was part-parametric and it was informed by the results from the earlier BL benchmarking experiments. One example of that was the omission of variations in pressure, the effect of which, in the range applicable, had been found to be minimal to the point of irrelevance.

Meanwhile, the retention of the catalytic effect in char from different BL/PO blends had already been demonstrated in a lab-scale study carried out at low heating rates in flameless conditions. However, the extent to which crucial parameters such as syngas composition, reactor temperature, sulphur distribution, carbon conversion and cold gas efficiency would vary in response to the dilution of fuel alkali content, which was brought about by the addition of pyrolysis oil, remained to be seen. These changes, and more, were investigated, quantified and assessed. The results from this study are presented in the second paper in this compilation.

Although the co-gasification runs continued at the plant following the completion of the above-mentioned study, the focus had shifted to the assessment of process stability at different blend ratios and the evaluation of performance variations under continuous multi-day operation. Several BL/PO
blends were gasified using two different grades of PO over the course of four long experimental runs, lasting at least six days each. By the time the gasification activities drew to a close in April 2016, the plant had been operated for over a thousand hours on blends with up to 20 wt.% PO, which corresponded to ~32% on an energy basis.

2.2 Gasification Setup
The oxygen-blown, pressurised entrained-flow gasifier that sat at the heart of the BLG process was originally developed by Chemrec AB and commissioned in September 2005[39]. It featured a centrally mounted burner with a co-annular nozzle at the top of the vessel. The nozzle was optimised for the feeding of preheated black liquor although, in its final years of operation, it was also used to successfully feed blends of black liquor and pyrolysis oil to a refractory-lined reactor vessel. The gasifier was pressurized at around 27-29 bar under standard operating conditions. At the nozzle outlet, the flow of BL exiting the annular nozzle was atomised by the O₂ issuing from the central nozzle to produce a syngas rich in CO and H₂ and a smelt containing carbonate and sulphide salts of alkali metals, which were returned to the nearby pulp mill for reuse. An overview of major process components and key media streams is shown in Figure 1, while a more detailed schematic of all the flows included in the mass and energy balances is provided under “Supplementary Information” in Paper I.

![Figure 1. The major process components and the key media streams.](image)

After exiting the reactor, both syngas and smelt passed through a quench tube where they were cooled by four diametrically opposite nozzles that sprayed condensate along the walls. The orientation and alignment of these nozzles determined the spray trajectory, which in turn influenced the cooling rate, and thus syngas composition, owing to the temperature dependence of gas-phase water-gas shift and hydrolysis reactions[40] (Paper I). After exiting the quench tube, the smelt was dissolved in a pool
made up primarily of water. The resulting liquid was called green liquor (GL) and the space occupied by the pool as well as region immediately above is hereafter referred to as GL dissolver. To avoid material build-up, the inner wall of the quench tube was wetted with a thin film of condensate called the primary film, which discharged into the GL dissolver. Meanwhile, syngas was cooled further by an additional set of nozzles on its way out of the quench tube, the so-called “secondary spray”, and bubbled through a water-lock before exiting the vessel.

Secondary spray emptied into a water-lock where it was joined by the run-off from a third set of nozzles which were used for cooling the lower face of the metal column that supported the reactor lining. A metal wall that separated the water-lock from the dissolver was indirectly cooled by a thin film of water called the secondary film, which drained into the bottom of the gas cooler. Note that the spatial locations of the aforementioned sprays and films can be found in Figure 2 of Paper I. The hot, wet syngas leaving the gasifier after quenching contained particles entrained in the flow. It was further cooled indirectly through heat exchange with water in a vertically mounted gas cooler containing two shell-and-tube heat exchanger modules in series. As a result, water vapour in the gas condensed and, together with the entrained particles, droplets fell down the exchanger tubes into a condensate reservoir that was used to feed the various different sprays and films. Plant control was configured to ensure that the level of gas condensate in the pool never falls below a minimum threshold. Excess flow was discharged to the GL dissolver from where it eventually exited the system as GL bound for the pulp mill. Hence, there were no waste streams and the setup reflected an arrangement that would be viable for use in commercial implementation with some modifications to the cooling system. In order to avoid sedimentation in GL dissolver, a water-sealed pump was used to keep the GL in circulation. Meanwhile, a separate water stream flushed the bottom of the vessel’s external level measurement gauge. Both these flows emptied into the GL dissolver. The bulk of the gasifier vessel was cooled by atmospheric air, while water was used for additional localized cooling of the burner nozzle and the bottom part of the reactor, which was also referred to as “cold support ring.”

Since the plant lacked the means to store and process large quantities of pyrolysis oil, a continuously-stirred day tank with a volume of 2.2 m$^3$ was built and commissioned before the start of the initial co-gasification experiments. It was later complemented by a larger tank, which was capable of storing more than 45 m$^3$ of PO for use in multi-day experimental runs. A pressurized mixer was mounted upstream of the gasifier in order to ensure comprehensive physical mixing of black liquor and pyrolysis oil, thereby avoiding pH and temperature gradients, which could adversely affect process performance. During operation, PO was taken from the tank, pressurized to the required pressure, and fed to the mixing vessel at the bottom, while the black liquor entered from the top. Together with oxygen, the blend that exited the mixer was fed to the gasifier through a co-annular nozzle at the top of the vessel. The co-gasification of the BL/PO blends did not require any modification to either the design of the nozzle or the operation of the existing gasifier feeding system.
2.3 Analytical Instrumentation, Sampling and Analysis Procedure

Since the BLG plant had originally been constructed for testing and development, it was equipped with extensive instrumentation for the measurement of pressure, mass flows and temperatures. Some of the instruments that were used in the experimental studies are described here briefly but note that the list is not comprehensive. A refractometer on the black liquor stream allowed the monitoring of variations in solids fraction, which was of great help in understanding real-time changes in process behaviour. The CH₄ content in syngas was monitored using an online Non-dispersive infrared sensor (NDIR). In addition to use in process control for monitoring variations in reactor temperature brought about by changes to the oxygen flow, it was also used as an indicator of flame stability. An array of seven thermocouples, grouped in three rows vertically along the reactor wall, allowed the measurement of temperature at different points in the reactor. Mass flows in BL, GL, oxygen and syngas streams were measured using Coriolis flow meters, while orifice flow meters were used for all other streams. Since the accuracy of flow measurement data was critical to the performance of reliable mass balances, syngas and green liquor flow meters were recalibrated for the black liquor validation experiments in September 2014. The resulting calibration constants were applied to all flow rates in the balance. More details on the calibration carried out for the co-gasification studies are provided under “Supplementary Material” in Paper II.

In order to ensure steady-state conditions, each operating point (OP) was in place for approximately twenty-four hours for the BL benchmarking study in September 2014 and for at least six hours in the part-parametric co-gasification study in June 2015. Consequently, the duration of all OPs was well in excess of both the gas residence time of a few minutes and the average liquid hydraulic residence time for of around 1.9 hours (see Paper I)[40]. Black liquor, green liquor, syngas and condensate samples were collected from all OPs in both the key studies mentioned above and from selected OPs in the other studies. All samples were generally taken immediately prior to switchover to a new OP. They were analysed at a number of laboratories and relevant information on measurement methods and standards is collated in Table 3 in Paper II. BL compositions were determined using averages of measured values from two samples on either end of the experimental runs, where possible. These averages were then adjusted for each OP using data from the refractometer to account for functions in the solid content. The heat capacity of BL, which was required for calculating enthalpy changes was estimated using a generalized empirical relationship developed by Zaman et al[41].

2.4 Performance Quantification and Assessment Parameters

2.4.1 Efficiency of Energy Conversion

The energetic efficiency of the gasifier was quantified using the concept of cold gas efficiency (CGE), which is broadly defined as the ratio between the chemical energy in syngas and the chemical energy
in the fuel from which it is derived. Since the production of syngas from biomass has historically been primarily aimed at combustion applications for power generation, CGE_{power} takes into account the heating value of all detectable and combustible syngas species including minor species such as H₂S, CH₄ and C₆H₆. CGE_{fuel} only considers the energy in CO and H₂. It is a better performance measure for cases that involve the upgrading of syngas to biofuels or biochemicals. CGE_{fuel+S-free} is calculated from the heating value of CO and H₂ in syngas and sulphur-free BL. In any application where the gasifier is integrated with a pulp mill, it would be required to supply high quality green liquor with sulphur in a reduced state (as H₂S) for re-use in the pulp recovery cycle. Hence, calculation of energy efficiency on a sulphur-free basis is considered the most representative parameter for evaluating performance in such an instance.

2.4.2 Efficiency of Carbon Conversion
In applications with only gaseous end products, carbon conversion efficiency is often defined as the ratio of carbon in syngas to that in the fuel. However, in an entrained-flow gasifier integrated with a pulp mill, this definition needs to be modified to account for the inorganic carbon in GL (GL TIC) that is recovered and reused at the pulp mill as a part of the recovery cycle. Syngas from the gasification of both pure BL and PO/BL blends is virtually free of tars[42]. Benzene is the only higher hydrocarbon that is regularly present in any notable amount and its concentration did not exceed 200 ppm for any of the OPs evaluated in the study. Such a concentration amounts to no more than 0.002% of fuel carbon input at standard conditions. Bearing this in mind and the cooling system set-up, all unconverted carbon ends up in GL. The efficiency of carbon conversion was thus defined as follows:

\[ \eta_{\text{carbon}} = \left(1 - \frac{m_{\text{GL TOC}}}{m_{\text{C,fuel}}} \right) \times 100 \] (1)

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

2.4.3 Fuel Classification
The characterization of fuels based on elemental constituents, as typified by Van Krevelen plots, is often carried out using molar H/C and O/C ratios. In a wide-ranging survey carried out in the early 1990s, the molar H/C and O/C ratios of biomass fuels were found to lie between 1-2 and 0.3-1, respectively[43]. The corresponding ranges were 1.2-4 and 0.4-1.1 in a more recent review of empirical models for the prediction of biomass heating value[44]. For reference, the H/C and O/C ratios of the black liquor used from the June 2015 co-gasification experimental study were 1.44 and 0.93, respectively. The corresponding figures for pyrolysis oil were 1.44 and 0.57. Similarly to coal, the difference in heating values between biomasses with low ash content has been correlated to
differences in O/C and H/C ratios[45]. At the same time, neither of these ratios provides an intuitive and explicit means of differentiating between fuels based on variations in inorganic content. Thus, for alkali-rich fuels like BL, a parameter such as alkali/C ratio, which decreases with increasing PO fraction, provides a more representative means of characterization. In this work, all fuel flows are classified in terms of their molar alkali-to-carbon ratio for quantitative comparisons, where required.

2.4.4 Relative Oxygen Content and λ
In combustion processes, variations in the amount of oxidising agent are often quantified by parameters such as air/fuel ratio, oxygen/fuel ratio and, in particular the oxygen-fuel equivalence ratio, $\lambda$. The reactor temperature has been shown to be a nearly linear function of $\lambda$ in entrained-flow gasification at steady-state conditions[46]. By definition, $\lambda$ does not explicitly take into account variations in fuel oxygen content[47]. This can conceal the role played by the oxygen native to a fuel that, in most instances, is also available to the gasification reactions taking place in the reactor. Since the oxygen content of biomass-based fuels varies, it can be instructive to use a truly feedstock-independent parameter, which explicitly takes into consideration the contribution of feedstock oxygen. Thus, in this study, the relative oxygen content (ROC) in a gasifier is used as a measure of the total available oxygen in the reactor. ROC, which has been used previously in studies on biomass gasification[48], is defined as follows[47]:

$$ROC = \frac{O_2_{\text{additional}} + O_2_{\text{fuel}}}{O_2_{\text{stoich}} + O_2_{\text{fuel}}}$$

(2)

In eq 2, $O_2_{\text{additional}}$ stands for added oxygen, $O_2_{\text{fuel}}$ represents the fuel oxygen content, and $O_2_{\text{stoich}}$ denotes the additional oxygen required for stoichiometric combustion.

2.5 Thermodynamic Equilibrium Modelling of Catalytic Co-Gasification
The third paper in this compilation is based on a study that assessed the usefulness and accuracy of unconstrained thermodynamic equilibrium modelling as a tool for the study and simulation of catalytic entrained-flow gasification of biomass-based feedstocks. In the first part of Paper III, the co-gasification of black liquor and pyrolysis oil blends was modelled using process and feed data from the June 2015 co-gasification study that is presented in Paper II. The results from the thermodynamic equilibrium calculations were compared with the experimental findings to assess the relevance and accuracy of the method as a viable tool for simulating catalytic entrained-flow gasification of varied biomass feedstock. In the second part, the gasification performance of the more general cases of both liquid and solid sodium-impregnated biomass was modelled for an assortment of fuel compositions. The compositions were obtained by varying the elemental O/C, H/C and Na/C ratios in carefully chosen ranges to obtain fuel mixes that were representative of real biomass feedstocks impregnated with alkali.

The thermodynamic equilibrium calculations (TECs) were carried out using the MATLAB-based SIMGAS model[49], which utilizes a non-stoichiometric approach in conjunction with the use of ideal
mixtures for both the gas and the inorganic smelt phase. The components included in the model are listed in Table 1. The model was initially developed at Chemrec AB as a part of their pressurized, entrained-flow black liquor gasifier development program and later improved at LTU[49]. More details can be found in a recent publication[49]. Since it was based on the oxygen-blown unit at the LTU Green Fuels plant, the ‘virtual’ gasifier used in the thermodynamic equilibrium simulations of catalytic co-gasification simulated an auto-thermal, pressurized process.

Table 1. Pure components included in the SIMGAS Gibbs energy minimization

<table>
<thead>
<tr>
<th>Gas</th>
<th>Solid/Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ (g)</td>
<td>Na₂CO₃ (l)</td>
</tr>
<tr>
<td>CO (g)</td>
<td>Na₂S (l)</td>
</tr>
<tr>
<td>CO₂ (g)</td>
<td>NaCl (l)</td>
</tr>
<tr>
<td>H₂O (g)</td>
<td>NaOH (l)</td>
</tr>
<tr>
<td>H₂S (g)</td>
<td>Na₂SO₄ (l)</td>
</tr>
<tr>
<td>CH₄ (g)</td>
<td>K₂CO₃ (l)</td>
</tr>
<tr>
<td>COS (g)</td>
<td>K₂S (l)</td>
</tr>
<tr>
<td>N₂ (g)</td>
<td>KOH (l)</td>
</tr>
<tr>
<td>KCl (l)</td>
<td></td>
</tr>
<tr>
<td>K₂SO₄ (l)</td>
<td></td>
</tr>
<tr>
<td>C (s)</td>
<td></td>
</tr>
</tbody>
</table>

One of the aims of the first part of the work was to study and compare the equilibrium temperature prediction for both pure BL and the PO/BL blends. Hence, for the validation and simulation of pilot plant data, the model was executed in a mode where heat loss was specified based on experimental measurements and the temperature was calculated by solving the energy balance over the gasification process. The inputs consisted of the temperature, flow and composition of the streams entering and exiting the reactor, namely, fuel, oxygen and a small amount of nitrogen. As the readings from the mass flow meter on the inbound nitrogen stream were clearly erroneous, the flows in produced syngas were used instead.
In the second part, a gasification temperature of 1050°C was specified, which meant that the amount of oxygen required to reach this temperature varied from case to case. All TECs were performed at 31 bar. The choice of values for some parameters was influenced by the wish to simulate cases that would mirror commercial-scale operation in an integrated biorefinery set-up. As a result, the heat loss through the reactor walls was set to 0.7% of fuel higher heating value (HHV) even though measurements show that the heat loss in pilot-scale can be as high as 6% of fuel HHV at a thermal load of ~ 2.8 MW. The desire to evaluate a broad spread of potential feedstock, and the breakdown of the compositions of likely catalytic gasification candidates meant that a H/C range of 1 to 2 and an O/C range of 0.4 to 1 were considered appropriate for use in determining the fuel mixes in the study. The elemental alkali/C ratio was varied between 0.01 and 0.45. This wide range of ratios was picked to include both the high[50] and the low[27] ends of the alkali-loading spectrum for fuels that have been mooted for entrained-flow gasification.

The calculations were performed at two different solids fraction, which permitted an evaluation of the effect of dry solids fraction on syngas composition and cold gas efficiency in the selected ranges. Since the unconstrained mode in SIMGAS was found to be able to model BL gasification with sufficient accuracy[49], its use was continued for the general case of catalytic biomass as well. In contrast to black liquor, most processed biomass feedstocks that are of interest to entrained-flow gasification, such as pine wood, oak bark and pyrolysis oil contain small to negligible amounts of nitrogen and sulphur. Consequently, all fuels were assumed to be composed of carbon, hydrogen, oxygen and sodium only, the latter of which represented alkali elements. Before performing the modelling, a survey of elemental composition-based empirical correlations was undertaken in order to identify suitable options, which are presented in Table 1 of the third paper. Based on the result of the survey and a subsequent benchmarking exercise, a correlation which explicitly took into account the ash content of the fuel was selected for use in the TECs.
3 Results and Discussion
This section provides an overview of the major results from the appended papers and a discussion of their significance. The papers relevant to each section are specified in parenthesis.

3.1 Overall Mass Balance
(Paper I and II)

The overall mass balance closure during the BL benchmarking study in September 2014 and the parametric co-gasification study in June 2015 did not deviate by more than 7%. The average closure was 104% in September 2014 and 97% in June 2015. Furthermore, of the 26 OPs in the multi-day co-gasification experimental runs from autumn 2015 and spring 2016 for which mass balance calculations were performed, 25 returned closures of 100±5%. In general, the closures did not appear to vary systematically in response to changes in reactor temperature, pressure or blend ratio. The numbers presented above underscore the relative stability of the process as well as the accuracy of control and measurement equipment. Both these factors greatly facilitated the identification, at least in part, of interesting trends in process outputs over the relatively narrow window available for varying phenomenologically interesting parameters such as flow rate, residence time and reactor temperature due to operational constrains.

Figure 2. The distribution of total mass flows entering the gasifier between black liquor (solid), pyrolysis oil (dashed vertical), oxygen (dotted diamond), water (dashed diagonal) and nitrogen (zig zag) for a selection of operating points encompassing a range of fuel blends and reactor temperatures between 2014-2016.
Figure 3. The distribution of total mass flows exiting the gasifier and crossing the system boundary between green liquor (dotted diamond) and syngas (upward diagonal) for a selection of operating points encompassing a range of fuel blends and reactor temperatures between 2014 and 2016.

The flow rate of water, which entered the gasifier through three separate streams, did vary to a certain extent between both individual OPs and in particular between experimental runs (Figure 2). These variations were caused both by the trade-off between operational considerations, green liquor strength and quality as well as a confluence of factors that were specific to the streams, such as an overestimation of GL flow in September 2014 and an underestimation of the “level measurement flow”. In spite of a calibration of the flow meter in question, it was this latter flow that was identified as the single largest cause behind the deviations of 3-6% in the mass balances of the parametric co-gasification experiments. It can be seen from the distribution of mass flows shown in Figure 3 that GL accounted for around 80% of the total outflows. Hence, the closure was sensitive to even small relative errors. Although it did exhibit short-term fluctuations, which are believed to be linked to the configuration of a control loop and scale build-up, with an hourly standard deviation of between 20-60 kg/hr, these corresponded to only 1-2% of the input flow.

3.2 Elemental Mass Balances
(Paper I and II)

The deviation in carbon balance closures (Figure 4) ranged between 5-6% for both pure black liquor and the blends across the experimental runs. Although the carbon balance is sensitive to errors in both flow measurements and elemental concentrations, the relative homogeneity of the closures for a wide range of OPs at different settings from experimental runs far apart in time does give some confidence
in the accuracy of the measurement. Fluctuations in the solids fraction of black liquor meant that the carbon input showed variations of up to 2% on a mass basis over the same, multi-day experimental run. Additionally, the use of an averaged BL solids composition in the mass balance was predicated upon the assumption that both the raw material used for pulping and the operational conditions would remain relatively stable throughout the experimental runs. Consequently, the elemental composition of BL solids was also not likely to vary significantly between OPs.

Figure 4. The fraction of carbon (a) entering the gasifier in black liquor (solid) and pyrolysis oil (upward diagonal) as well as the distribution of carbon flows (b) exiting the gasifier in green liquor (dotted diamond), carbon monoxide (diagonal stripes), carbon dioxide (solid) and methane (dashed horizontal) for a selection of operating points encompassing a range of fuel blends and reactor temperatures between 2014-2016. Compared to the carbon balance closure, the sulphur balance closure (Figure 5) showed greater variation between experimental runs. The black liquor validation experiments from September 2014
yielded excellent closures with a maximum deviation of 4%. In comparison, with a mean closure of 104%, a standard deviation of 7.4% and a maximum deviation of 19%, the sulphur balances for the OPs in the June 2015 co-gasification experiments closed less well. However, in both cases, the deviations in the closures, as well as those of sodium and potassium were attributed to the presence of systematic errors, principally in the measurements of elemental compositions in green liquor, which have a measurement uncertainty of 10%.

Figure 5. The distribution of outbound sulphur between green liquor (dotted diamond) and hydrogen sulphide (solid) for a selection of operating points encompassing a range of fuel blends and reactor temperatures between 2014 and 2016.

3.3 Energy Balance
(Paper I and II)

The distribution of the sensible and chemical energy (on a HHV basis) in both the inbound and outbound streams is summarised on Figures 6 and 7 for a selection of fuel blends and reactor temperature. The deviation in the energy balance closures, which are shown on Figure 7 were pretty consistently in the range of 4-6% across the experimental runs. It was contributed to by several factors, namely, errors in the measurement of GL flow, the choice of ethanol as representative of GL TOC, and the uncertainty surrounding the completeness of sulphur reduction.
Figure 6. The distribution of energy entering the reactor between black liquor (solid), pyrolysis oil (dotted diamond) and the sum total of the sensible heat carried in by the flow streams (upward diagonal) for a selection of operating points encompassing a range of fuel blends and reactor temperatures between 2014-2016.

As expected, the heating value of the fuels accounted for most of the energy input. Most of the rest was present in BL as it is pre-heated to 140°C and the remainder is carried in by the three water...
streams. Since the experiments were carried out in pilot-scale, the heat loss through the gasifier walls varied between 6-7% of fuel HHV at a thermal load of ~ 2.8 MW. In a commercial unit, it is projected to be around 0.7% of fuel higher heating value. The “BL Std. (April 2016)” OP in Figure 7 represents a larger thermal load of 3.3 MW and the heat loss at this OP was proportionally smaller. Note that the heat loss was calculated on the basis of actual flows and measurements for the black liquor validation experiment run. However, due to thermocouple malfunction, temperature data for the water cooled streams was not available for the parametric co-gasification experiments and an averaged value was used instead.

Most of the energy in the fuel leaves the gasifier as syngas, which is cooled down to around 30 °C in the two-stage counter-current condenser. The cooling load is significant and in a commercial implementation, a significant portion of the latent and sensible heat borne by GL and the various cooling flows would be recovered and utilised to produce process steam for the integrated pulp mill. While GL contained minor amounts of unconverted organic carbon, which represented about 1-2% of the chemical energy input, most of the chemical energy in the flow was due to the presence of sulphur in reduced form.

3.4 Effect of Blend Ratio on Syngas Composition
(Paper II)

Syngas from the blends was as clean as that from pure black liquor and benzene was the only higher hydrocarbon that was consistently present in amounts greater than 20 ppm. The effect of blend ratio on the yields of the major gas species, namely, H2, CO and CO2 was evaluated in Figure 8 by plotting the changes in their flow rates against changes in the fraction of PO in the fuel during two different experimental runs at a constant thermal load. In both cases, an increase in the fraction of PO in the fuel led to a nearly proportional increase in the amount of CO even as the amount of CO2 saw an equally clear swing in the opposite direction. Note that owing to small differences in fuel compositions, the actual flow rates differed somewhat between the experimental runs for the same load and blend ratio. The June 2015 experiments saw a steady increase in the flow rate of H2 with blend ratio, whereas in the March 2016 experiments, the flow rate recorded a dip at the 15% PO blend before recovering to a higher value.

Since the increase in the flow rates with blend ratio was not as pronounced for H2 as it was for CO, the H2/CO ratio actually decreased from 1.36 for pure BL to 1.23 for the 20% PO blend in the June 2015 experimental run. The increase seen in the CO and the H2 yields with an increase in blend ratio can be attributed to the reduction in reactor thermal ballast that is brought about by a decrease in fuel inorganic content. Consequently, less heat needs to be generated to bring the reactor contents to gasification temperature and less CO and H2 are consumed as a result.
The shift in the division of carbon between syngas and green liquor with an increase in blend ratio was so pronounced that in June 2015, the 20% PO blend actually returned a higher combined yield of CO and CO₂ compared to pure BL, in spite of there being 5%-points less carbon in the fuel on a mass basis. The net effect of the changes in the yields of the major components was such that the change in blend ratio from 0 to 20% corresponded to a 17% reduction in the additional oxygen demand per mole of H₂+CO produced.

Figure 8. The change in syngas CO (circle), CO₂ (star) and H₂ (square) with blend ratio (0-20%) at approximately constant thermal loads and syngas methane content during experimental runs in (a) June 2015 and (b) March 2016.

Figure 9. The change in syngas H₂S (diamond) and CH₄ (triangle) with blend ratio (0-20%) at approximately constant thermal loads and syngas methane content during experimental runs in (a) June 2015 and (b) March 2016. Note that the H₂S concentrations for the 10% PO operating points in March 2016 were not available.

The decrease in fuel sulphur content with an increase in blend ratio resulted in a corresponding decrease for sulphur released as H₂S. A characteristic feature of pressurized entrained-flow black
liquor gasification is the division of the sulphur in the fuel between the gas and the liquid phases. The so-called sulphur split, which is defined as the ratio of the amount of sulphur in syngas to the amount of sulphur in the fuel is sensitive to operational parameters such as temperature, pressure and residence time. On the one hand, the availability of sulphur in gas phase enables recovery in a separate stream, if desired. At the same time, this split also promotes the formation of alkali carbonates, which would increase the consumption of burnt lime in the causticisation unit at the pulp mill (see the section titled “Green Liquor” in Paper I).

\[ \text{Na}_2\text{S}(l) + \text{H}_2\text{O}(g) + \text{CO}_2(g) = \text{Na}_2\text{CO}_3(l) + \text{H}_2\text{S} (g) \rightarrow \Delta H_r = -169.8 \text{ kJ/mol (1)} \]

Figure 10b shows that sulphur split decreased with an increase in temperature for both pure BL and the blends. Such a change would be expected according to Le Chatelier’s Principle, although it is likely limited in its extent by the reaction in Eq. 1 being in partial equilibrium only.
3.5 Effect of Reactor Temperature on the Syngas Composition of a 15% PO blend (Paper II)

A comparison of the effect of temperature on the syngas composition of pure BL and a 15% PO blend from the June 2015 experimental run (not shown; see Figure 4 in Paper 2) makes it clear that the composition of syngas from unblended BL and the 15% PO blend exhibited largely similar behaviour in response to changes in temperature. However, the 15% blend showed noticeably less benzene than black liquor at nearly the same CH$_4$ flow rate and the difference in the benzene yield from the two fuels appeared to increase with temperature. It is also of some interest to see that the flow rates of the major gas components for six OPs encompassing four different compositions show a partial correlation with ROC to varying degrees (see Figure 4a in Paper II. It lends some support to the belief that ROC can be useful as a tool for predicting yield trends of major syngas species from ash-free biomass feedstocks for varying composition and gasification temperature.

Similar to the case of sulphite thick liquor[51], Kraft black liquor[52] and several solid biomass feedstocks[17], the CH$_4$ content in syngas from the blends also showed an excellent correlation with reactor temperature measurements, in particular those from the upper and middle arrays of thermocouples which were located closer to the flame. However, in comparison with BL, the 15% PO blend yielded slightly higher temperatures at all measurements positions for approximately the same CH$_4$ content. This trend was also predicted by thermodynamic equilibrium calculations of black liquor and pyrolysis oil co-gasification (see Figure 1 in Paper III), although the inability of the model to correctly predict CH$_4$ concentrations was responsible in part for an over-prediction of the difference.

3.6 Composition of Gasification GL and the Effect of Blend Ratio (Papers I and II)

The concentrations of the most important ions and elements in the GL produced from the gasification of pure BL in September 2014 and the PO/BL blends in June 2015 are summarised in Table 3 of the first paper and Table 4 of the second paper, respectively. The first of these two tables also includes equivalent data for typical recovery boilers. A look at it reveals that the composition of gasification GL produced from both pure BL and the PO/BL blends differs from that of typical recovery boiler in some important ways. Firstly, typical recovery boiler GL contains OH$^-$ ions, whereas in the gasifier, these ions react with the CO$_2$ in syngas to form bicarbonate ions. Secondly, the gasification GL has a lower concentration of sulphur since, as discussed in the previous section about one third of the sulphur in the fuel is released as H$_2$S, which also leads to an increase in the concentration of carbonate ions. Thirdly, analysis of GL samples from the September 2014 revealed the presence of formate ions, which were hypothesized to have formed from the reaction of syngas CO with aqueous NaOH in the GL dissolver. This formation pathway was shown to be thermodynamically feasible in a simulation of GL dissolver that was carried out in ASPEN HYSYS using the OLI electrolyte database (see the
“Supporting Information” in Paper 1 for more information). The carbon in the formate concentrations measured in GL during the September 2014 experimental run were found to be the equivalent of between 0.6-1% of the carbon in syngas and no more than 0.4% of the carbon in BL.

Table 4 in the first paper presents a breakdown of the inorganic and organic carbon fraction in green liquor samples from the September 2014 experimental run. The results showed that the carbon content of GL sludge was almost vanishingly small and predominantly inorganic in nature. The vast majority of the carbon in GL was thus present in dissolved form. Between 90-95% of this carbon was inorganic in nature (see the section titled “Green Liquor” in Paper I). The carbon split between green liquor and syngas is ultimately decided by the alkali metal content of the fuel, which decreased in inverse proportion to the amount of pyrolysis oil in the blend, thereby leading to a corresponding decrease in the proportion of fuel carbon in green liquor.

![Figure 11. The effect of blend ratio (0-20%) on sludge (square), TOC (triangle) and TIC (circle) concentrations in green liquor during the June 2015 experimental run.](image)

It can be seen from Figure 11 that, as expected the concentration of total inorganic carbon (TIC) decreased with increasing PO fraction. GL sludge fractions and TOC concentration in the GL filtrate from both the blends and BL were comparable and did not show any systematic variation. The carbon found in formate ions constituted 23-41% of the TOC in the GL filtrate from the blends and 24-49% from BL. The rest of the TOC is believed to be composed mainly of low-molecular weight tars that condensed during gas cleaning and quenching.

### 3.7 Sulphur Reduction Efficiency
(Papers I and II)
Since any sulphur that is present in a form other than Na₂S or K₂S does not play an active role in the Kraft cooking process, from the perspective of integration in a pulp mill, it is important to recover as much sulphur as possible in the form of sulphide. An earlier study on the gasification of spent sulphite liquor that was also carried out at the LTU Green Fuels pilot plant had reported reduction efficiency values of 100% within measurement uncertainty limits[51]. For comparison, typical values for recovery boilers are 90-95%. Due to the results from the aforementioned study, sulphur reduction efficiencies were not calculated in the black liquor validation experimental run in September 2014. However, interestingly and somewhat unexpectedly, as seen from Table 4 in the 2nd paper, the HS⁻ concentrations in GL were consistently lower than total sulphur concentration for both BL and the blends from the June 2015 experiment. It is worth bearing in mind that the methods used for the determination of HS⁻ and total S concentrations have specified relative measurement uncertainties of 15% and 10%, respectively. These are of the same order of magnitude as the differences between their measured concentrations.

The GL produced at the pilot plant was extremely sensitive to oxidation during sample preparation, which made the quantification of reduced forms of sulphur, such as sulphide ions, very difficult. This meant that it was not possible to carry out a complete characterization of sulphur species. Having said that, given the high reduction efficiencies seen previously and the large measurement uncertainties of the values, the deviation may be down to systematic analysis-related errors alone. Nonetheless, in light of the above results and given the significance of sulphur recovery to pulp mill integration, further investigating the possibility of the presence of non-reduced forms of sulphur in gasification GL would be of interest.

3.8 Carbon Conversion Efficiency
(Papers I and II)

It can be seen from Figure 12, which plots the carbon conversion efficiencies of all the OPs from the June 2015 co-gasification experiments as a function of their alkali/C ratio that carbon conversion did not vary systematically with either blend ratio or temperature. Instead, the gasification of both pure BL and the PO/BL blends in the June 2015 experimental run yielded ηC efficiencies in the range 98.8-99.5%. These efficiencies were comparable to those that were obtained during the gasification of pure BL in the September 2014 experimental run (see Table 9 in Paper I for more information). In all the experimental runs evaluated and presented in this thesis, the very high degree of conversion was also implicitly supported by the absence of any detectable unconverted char in GL. Note that if the carbon present in formate were to be considered “converted” for the purpose of efficiency calculation, the values presented above would increase by a further 0.2%.
3.9 Effect of Blend Ratio and Reactor Temperature on Cold Gas Efficiency

(Paper II)

In energetic terms, the value of increasing the PO fraction at a constant thermal load is captured well by Figure 13, which depicts the change in CGE (on an LHV basis) with an increase in blend ratio for the June 2015 experiments. In comparison with BL, the 20% PO blend yielded a 7%-point higher CGE_{Fuel}, a 7%-point higher CGE_{Power}, and a 5%-point higher CGE_{Fuel+S-free}.

Figure 13. CGE_{Power} (triangles), CGE_{Fuel} (circles) and CGE_{Fuel+S-free} (squares) on LHV basis for (a) the different fuel blends at standard temperature and (b) the 15% PO blend at varying temperatures.
The changes in CGE_{fuel} with blend ratio mirror the changes in the combined flow rate of CO and H₂ with the same parameters. Meanwhile, the decrease in the H₂S fraction in syngas with an increase in PO fraction meant that while it accounted for, on average, approximately 5% of LHV_{Power} in syngas from pure BL, the figure dropped to only 3.4% in the syngas from the 20% PO blend. On average, there was a difference of around 10-11%-points between CGE_{fuel} and CGE_{fuel+S-free} values.

It should be noted that CGE_{fuel+S-free} is computed as the ratio of syngas LHV_{fuel} to fuel LHV_{S-free}, which is influenced by variations in the sulphur content of the fuel. Given that unblended black liquor has a low heating value to begin with due to its high moisture and inorganic content, this difference illustrates the extent and the significance of the energy “penalty” associated with the need to regenerate vital pulping chemicals such as Na₂S and K₂S for reuse in the pulp mill. Seeing as the recovery of these pulping chemicals is central to the integration of an entrained-flow gasification based biorefinery concept at a modern pulp mill, it is believed that CGE_{fuel+S-free} is a more representative parameter for technological and techno-economic comparisons.

### 3.10 Effect of Natural Variations in BL on Process Performance

Even though the composition of BL solids remained constant in the short run, natural variations do occur in the long run, and the carbon content of the liquors were found to vary by up to 2-3%-points between experimental runs that were a year apart. Likewise, the solids fraction can also fluctuate, as illustrated in Figure 2 of paper 1. The resulting variations in fuel composition can have a significant influence on external oxygen demand and cold gas efficiency.

![Figure 14](image-url)

Figure 14. The spread of selected CGE_{fuel} values from four different experimental runs between June 2015 and April 2016 for the same nominal blend ratios at nearly constant thermal load and syngas methane fraction. Pure black liquor is denoted by solid diamonds, 10% PO is denoted by hollow squares and 20% PO is denoted by hollow triangles.
This is illustrated on Figure 14, which shows the spread in CGE values because of naturally occurring variations in fuel compositions at the same nominal blend ratio, thermal load and syngas methane fraction. The OPs plotted on the figure were chosen from four different experimental runs between June 2015 and April 2016 because of being virtually identical in terms of their operational settings. Yet, both the alkali/C ratios and in particular the CGEs, which vary by as much as 4%-points, show considerable variations between the experimental run.

3.11 Validation of Predicted Syngas Compositions from Thermodynamic Equilibrium Calculations

Figure 15. A comparison of experimentally determined (solid) flow rates of (a) CO (circle) and CO2 (diamond) as well as (b) hydrogen (square) in cold gas with their predicted (hollow) counterparts at reactor exit.

Figure 15 compares the predicted flows of the major syngas species, namely, CO, CO2 and H2 with experimental data from the co-gasification study that is presented in Paper II. The figure shows that the model successfully predicted the direction of change in CO and CO2 with increasing blending ratio. The prediction of H2 flow rate disagreed with the measured value by up to 10%; however, the disagreement did not exhibit any systematic variations with increasing blend ratio. The predicted data presented in the above figure represents syngas compositions at reactor exit. It does not take into account reactions and interactions that take place during syngas cooling[42]. It was possible to quantify changes in composition due to some of these interactions, such as the reaction of CO2 with alkali hydroxides and its absorption by GL to form carbonate as well as the absorption of CO by GL to form formate. However, the final composition is principally set by the water-gas shift reaction as the gas continues to cool down in the quench tube. As the temperature of the syngas fall due to radiative cooling, the equilibrium of the reaction favours the production of CO2 and H2 at the expense of CO and H2O. This was not included in the model and could not therefore be quantified.
Figure 16 presents a comparison of the total carbon in the predicted CO and CO\textsubscript{2} flow rates with experimental data as well as CO and CO\textsubscript{2} that were adjusted to take into account the interactions outlined in the previous paragraph. These results reveal two important points. First, the disagreement between the experimental and the uncorrected flow rates is limited to \(\sim 0.5\) kmol/hr at all the OPs and it is not systematically affected by blend ratio. To put this difference in context, it equates to between 3-5\% of the total carbon input for both pure BL and the blends, which is in the same range as the discrepancy in the experimental carbon balance over the gasifier. Second, an adjustment of the predicted flows to take into account reactions and interactions during cooling reduces the difference between the experimental and the predicted values to \(\sim 0.2\) kmol/hr or around 1\% of the total carbon input. The above analysis demonstrates that TECs may be used to predict the composition of the major components in cold syngas from alkali-catalysed biomass blends to a high degree of accuracy provided any reactions and interactions during syngas cooling are accounted for in the analysis.

![Figure 16](image_url)

Figure 16. A comparison between the experimental (solid diamond) and predicted (hollow) flows rates of carbon in syngas for both the uncorrected (circle) and corrected (triangle) cases. The corrected case takes into account the absorption of CO and CO\textsubscript{2} in GL and the reaction of CO\textsubscript{2} with alkali hydroxides to form alkali carbonates.

3.12 Validation of Predicted Equilibrium Temperature
(Paper III)

The effect of an increase in fuel PO fraction on both predicted and measured temperatures is plotted in Figure 17. It can be seen from Figure 17 that the predicted temperature increased nearly proportionally with increasing fuel PO fraction. In contrast, the measured temperature from the thermocouple at the bottom of the reactor remained constant at all blend ratios. Readings from thermocouples in the middle and near the top of the reactor (see Appendix A1 under “Supporting Material” in Paper III) also showed a similar trend, albeit at slightly higher temperatures. The differences between measured and
predicted temperatures reflect the fact that the former are not true measurements of the gas temperature. Besides the radiation from the flame, the temperature of both the gas and the ceramic lining also influences the readings. Furthermore, some of the difference also arises as a result of mispredictions of the CH$_4$ content by the model.

Figure 17. A comparison of predicted (diamond, triangle and circle) equilibrium temperatures for both black liquor (hollow) and black liquor/pyrolysis oil blends (solid) with an averaged measurement from the bottom thermocouple in the reactor. The circles joined by the dotted line represent a pyrolysis oil solids composition with 4%-points less oxygen.

However, the variation in the predicted temperature with increasing blend ratio cannot be attributed to differences arising from the underestimation of methane by the model since both the BL and the blends had very similar CH$_4$ flow rates of between 0.3 kmol/hr and 0.4 kmol/hr (see Figure 9a). These numbers corresponds to a CH$_4$ volume fraction of 1.1-1.2% in cold syngas. However, it has been shown that predicted temperatures can be very sensitive to relatively small variations in fuel composition[49]. Since the predicted and the measured temperatures lay quite near each other for the BL only OPs, compositional variations in BL alone could not explain the increase in predicted temperature with blend ratio. Two potential causes were identified: errors in the measurement of (a) moisture content and (b) solids composition. An analysis of the sensitivity of the predicted temperature to variations in PO moisture content showed that errors in the determination of moisture content are not likely to have contributed significantly to the over-prediction of equilibrium temperature.

However, the predicted temperature rose or fell by ~ 70°C for each 2%-point increment change in the oxygen fraction of PO solids. Such an increment corresponded to a decrease of 0.35%-points in the carbon content of the 20% PO blend. Given that the discrepancy in carbon balance closures ranges
between 2-5%-points based on published experimental (see Paper I), these variations would have little impact on the carbon mass balance and likely would not be picked up in an experimental study. The dotted line joining the three circles on Figure 17 showed the predicted temperatures for a PO solids composition with 4%-points less oxygen (see the section titled “Predicted Equilibrium Temperature in Paper III for further discussion). It shows a much better agreement with the measured temperatures and the difference between the two now mirrors that for the three BL points. These results hint at an underestimation of the carbon and hydrogen content in PO solids due to errors in the elemental analysis and highlight the sensitivity of predicted temperature to variations in the composition of PO.

3.13 Thermodynamic Equilibrium Modelling of Catalytic Biomass Gasification (Paper III)

3.13.1 Cold Gas Efficiency
An overview of the cold gas efficiencies (on a LHV basis) of liquid and solid biomass composition over the complete range of the elemental ratios simulated shows that the highest efficiencies were achieved at a H/C ratio of 1.1 and an O/C ratio of around 0.5.
Figure 18. The cold gas efficiencies of the simulated data points on a lower heating value (wet) basis over the full range of O/C and Na/C ratios analysed in the study at H/C ratios of 1.2, 1.5 and 1.8 and fuel solids fractions of 0.75 and 0.95. Selected fuels are marked on the plots for illustration and ease of comparison.

Compositions that had a lower O/C ratio produced small amounts of unconverted carbon, which indicate that fuels such as lignin that have low oxygen to carbon and hydrogen to carbon ratios need greater amounts of added oxygen to reach complete carbon conversion at the specified temperature of 1050°C. It can also be seen from Figure 18 that the CGEs for the wet fuels were ~ 6%-points lower than those for the solids fuels. The energy penalty for liquid feeding is thus similar in scale to that incurred by the addition of an alkali amount to solid biomass that yields an alkali/C ratio of around 0.25. Although the differences in the elemental ratios between some of the fuels are not large, the plots provide some indication of the incremental reduction in CGE (and HHV) due to the presence of alkali in different ionic concentrations.
3.13.2 H₂/CO Ratio in Syngas
There was a striking difference in the H₂/CO ratios of the liquid and solid cases (Figure 12). Compared to the former, the latter returned values that were lower by at least a factor of one-third. Consequently, while the CGE of 50/50 PO/BL was ~ 6% lower than that of 1M NaOH, the H₂/CO ratio was more than 40% higher, which translates into a significantly lower load for the shift reactor in a methanol synthesis application. These results show that the feedstock compositions that yielded the best cold gas efficiencies also produced syngas with a H₂/CO ratio that is sub-optimal for upgrading to biofuels and requires large shift loads.

Figure 19. The H₂/CO ratios in cold raw syngas over the full range of O/C and Na/C ratios analysed in the study at H/C ratios of 1.2, 1.5 and 1.8 and fuel solids fractions of 0.75 and 0.95. Selected fuels are marked on the plots for illustration and ease of comparison.
4 Conclusions and Recommendations for Future Work

The purpose of the experiments presented in this work was to study, quantify and understand the co-
gasification of black liquor and pyrolysis oil in pilot-scale for a range of process settings within the
gasifier’s operational envelope. The aim of the modelling work carried out in conjunction with the
above was to investigate catalytic entrained-flow gasification of biomass for a wide-range of elemental
compositions using thermodynamic equilibrium calculations.

Syngas from pilot scale gasification of both pure black liquor and the pyrolysis oil/black liquor blends
was virtually tar-free. The carbon conversion efficiency of both pure BL and PO/BL blends was in the
range 98.3-99.5%, and it did not vary systematically with increasing blend ratio. This shows quite
clearly that the addition of up to 20% PO on a mass basis does not degrade the catalytic activity of the
alkali present in black liquor. The decrease in fuel inorganic content with increasing PO fraction
resulted in a) an increase in cold gas efficiency by about 5%-units and b) more dilute green liquor
(GL). The composition of syngas from unblended BL and the 15% PO blend exhibited largely similar
behaviour in response to changes in temperature; in both cases, the “standard” temperature setting
appeared to represent the optimum for biofuel production. The fraction of sulphur that ends up in the
syngas was somewhat higher for the PO/BL blends than for BL. Due to analytical difficulties the
sulphur reduction efficiency was uncertain.

In summation, the results from the parametric study and the long duration experimental runs indicate
that the equipment developed for BL gasification can also be used for the co-gasification of BL and
PO if a PO feeding system and a BL/PO mixer is added. No other changes to the equipment appear to
be necessary, which means that a gasifier with a similar set-up may be used flexibly for the
gasification of BL only, blends of BL and PO as well as potentially other suitable liquid biomass
feedstocks.

The validation of the equilibrium model with experimental data from co-gasification of black liquor
and pyrolysis oil gasification showed that the syngas and the smelt compositions from the blends with
up to 20% PO were comparable in accuracy to corresponding figures for pure black liquor at all blend
ratios. Thermodynamic equilibrium calculations of catalytic entrained-flow gasification showed that
nearly complete carbon conversion at low temperature (1050°C) could be achieved by both solid and
liquid alkali-catalysed biomass feedstocks with elemental O/C and H/C ratios in the range 0.5-1 and 1-
2, respectively. Solid fuel compositions with low H/C ratios and an O/C ratio of around 0.5 yielded the
highest cold gas efficiencies of around 86% on a LHV (wet) basis. Liquid feedstocks produced syngas
that was richer in H₂ and the compositions of solid and liquid fuels differed by at least a factor of one-
third. The CGE of 50/50 PO/BL was ~ 6% lower than that of 1M NaOH woodchips, which had
comparable O/C and H/C ratios but a 50% difference in their alkali/C ratios. It is believed that the
characterization of the performance of gasification fuels based on molar elemental ratios offers a
useful visual aid for comparing cold gas efficiencies, syngas compositions, added oxygen use and any
other parameters that may be of relevance in process design and techno-economic evaluations.

Based on the above findings, further experimental work in the area of entrained-flow catalytic co-
gasification of PO and BL is needed on (i) method development for better characterization of GL
TOC, (ii) quantification of the effect of long-term variations in fuel composition on process
performance, and (iii) study of the sulphur chemistry in GL and the syngas cooling system. For the
development of a generic catalytic biomass gasification process, further work is required to
demonstrate and study catalytic entrained-flow gasification of both liquid and solid fuels in both lab
and pilot-scale to generate representative data for improved kinetic and techno-economic modelling.
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Paper I

Performance of a Pilot-Scale Entrained-Flow Black Liquor Gasifier
Performance of a Pilot-Scale Entrained-Flow Black Liquor Gasifier

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Supporting Information

ABSTRACT: Pilot-scale entrained flow gasification experiments were carried out at the 3 MWth LTU Green Fuels black liquor gasification (BLG) plant, using ~140 tons of Kraft black liquor (BL) with a dry solids content of ~73.5%. Comprehensive mass and energy balances were performed to quantify process performance under varying pressure, load, and oxygen/fuel ratio. Carbon conversion efficiency of the BLG process was 98.3%–99.2% and did not vary systematically in response to process changes. The unconverted carbon is almost exclusively present as dissolved organic carbon in the green liquor (GL) stream. GL is an aqueous solution of sodium carbonate and sodium sulfide used to recover the inorganic pulping chemicals present in BL for reuse in the pulp mill. A small fraction of syngas CO is converted to formate ions dissolved in GL through reaction with hydroxide ions. Unconverted carbon present in GL solids is insignificant. Syngas produced is subsequently upgraded to methanol and dimethyl ether (DME) in an integrated fuel synthesis facility. Concentration of H₂ in syngas is not significantly affected by operating point changes in the domain investigated, while CO and CO₂ concentrations are. Syngas hydrocarbon concentration values are typically in the single-digit parts per million (ppm) with the exception of CH₄, which was present at 16–127 ppm. CH₄ is present at 0.5%–1.2%, with lower concentrations at higher temperatures, and shows good correlation with C₂H₆. A quantity of 24%–27% of BL sulfur ended up in the syngas as 1.5%–1.7% H₂S and 64–72 ppm COS. Cold gas efficiencies (CGEs) on a lower heating value (LHV) basis, when including syngas CH₄, were 52%–55% and decreased at higher temperature. CGEs on an LHV basis, when considering only H₂ and CO with a sulfur-free BL heating value relevant for catalytic syngas upgrading, were 58%–60% and showed the opposite temperature dependence. Good mass and energy balance closures show the figures presented to be reliable. The results obtained from this study demonstrate process stability at varying operating conditions and can be further used for techno-economic analysis and design purposes.

INTRODUCTION

Spent cooking liquors from Kraft and sodium sulfite pulping processes have long been combusted in Tomlinson-type recovery boilers to recover pulping chemicals, generate electricity, and produce process steam. However, a quest for improvement in energy efficiency and a desire to decrease the use of fossil fuel-based power generation created increased interest in gasification as a promising alternative during the last decades of the 20th century. Recent years have seen a shift in the focus of research and industry attention to the transformation of pulp and paper mills into gasification-based biorefineries for the production of primarily liquid motor fuels. A range of concepts have been proposed, of which the pressurized oxygen-blown entrained-flow black liquor gasification (BLG) variant developed by Chemrec AB has come close to commercialization.

In a BLG-based biorefinery concept, the conventional recovery boiler is replaced with a gasifier to produce clean syngas and recover inorganic pulping chemicals. BLG is a pressurized entrained-flow process associated with elevated reactor temperatures and a gas residence time in the order of seconds. This allows for very high conversion efficiencies and, aided by the use of a water quench in combination with a counter-current condenser with an outlet temperature of ~30 °C, leads to the production of clean, tar-free syngas.

Most of the carbon in the fuel ends up in syngas but a significant fraction leaves the gasifier bound to an alkali carbonate melt and its recovery is an integral part of the pulping cycle. Syngas produced thus may subsequently be upgraded to biofuels while the recovered pulping chemicals are returned to the pulp mill as aqueous green liquor (GL).

Gasification of Kraft black liquor (BL) has been demonstrated for more than 25,000 h at a 3 MWth pilot plant in Piteå, Sweden, which was commissioned in 2005. It is currently owned and run by Luleå University of Technology. Since the startup of an adjoining fuel synthesis facility in 2011, syngas from the process is upgraded first to methanol and subsequently to dimethyl ether (DME). From its inception, the pilot plant has been used to carry out research on different aspects of BLG, as well as test the process performance of a feedstock consisting of a liquor from a sodium sulfite-based biorefinery. Recent work in the pilot plant has focused on the cogasification of BL and pyrolysis oil.

Previous studies on the pilot-scale BLG process have included the effect of gasifier and quench operating conditions on syngas composition and energy efficiency, as well as syngas purity, with respect to, e.g., tar and particles. Complete mass and energy balances have been published only for gasification of a feedstock from sodium sulfite-based biorefining. No complete balances have been published for gasification of Kraft BL, which is the most important fuel for the process. Moreover, hitherto published sulfite liquor mass and energy balances have been carried out using estimates of green liquor and syngas flow rates, because of unavailability of reliable mass flow data.

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Nearly complete carbon conversion has previously been reported for a feedstock from sodium sulfito-based biorefining, grounded, in part, on the absence of observable char in GL.\textsuperscript{11} However, no quantitative estimation of carbon conversion has been presented. Similarly, the organic content in GL, which is important for chemical recovery in the pulp mill, has not been published for Kraft BL gasification.

The study presented in this paper is based on an experimental campaign carried out using \(\sim140\) tons of Kraft BL, corresponding to \(\sim5\) days of continuous operation, from the nearby pulp mill. Specific study objectives were:

(a) to determine experimentally concentrations of key process elements in all streams entering and exiting the system, including organic and inorganic carbon fractions in green liquor;
(b) to perform comprehensive mass and energy balances using the measured values under several steady-state process conditions within the gasifier’s operating envelope;
(c) to quantify process carbon conversion and cold gas efficiency using the balances; and
(d) to identify previously undiscovered process phenomena.

An additional objective of the work was to carry out comprehensive benchmarking of the BLG process performance for use as an input to techno-economic analyses and a point of...
EXPERIMENTAL SECTION

Process Description. A detailed account of BLG, including plant setup, can be found in the literature.7 In recent years, some minor modifications have been made to improve performance. These include realignment of the cooling spray heads in the quench and removal of the external purge stream where gas condensate was released into a flash vessel. Figure 1 provides an overview of the major process components and all the media streams crossing the gasifier and gas cooler system boundary.

The oxygen-blown, pressurized entrained-flow gasifier that sits at the heart of the process features a centrally mounted burner with a coannular nozzle at the top of the vessel. It is used to feed BL, O2, and a small amount of N2 to a ceramic-lined reactor, pressurized at ∼27–29 bar under standard operation conditions. BL is atomized by O2 at the nozzle outlet; subsequent reactions lead to the production of smelt and hot syngas. An array of seven thermocouples, grouped in three rows vertically along the reactor wall, allows measurement of the temperature profiles.

Gasification products leave the reactor at the bottom and enter a quench tube, where they are cooled by two diametrically opposite nozzles spraying condensate along the walls. The spray trajectory influences the cooling rate and, consequently, syngas composition, because of the temperature dependence of gas-phase water–gas shift and hydrolysis reactions.1 Smelt from the reactor falls and dissolves in the heart of the process features a centrally mounted burner with a cooler system boundary.

The oxygen-blown, pressurized entrained-flow gasifier that sits at the heart of the process features a centrally mounted burner with a coannular nozzle at the top of the vessel. It is used to feed BL, O2, and a small amount of N2 into a ceramic-lined reactor, pressurized at ∼27–29 bar under standard operation conditions. BL is atomized by O2 at the nozzle outlet; subsequent reactions lead to the production of smelt and hot syngas. An array of seven thermocouples, grouped in three rows vertically along the reactor wall, allows measurement of the temperature profiles.

The secondary spray flow empties into a water lock, where it is joined by runoff from a third set of nozzles, which are used for cooling the lower face of the metal column supporting the reactor lining. A metal wall separating the water lock and the dissolver is indirectly cooled by a thin film of water called the secondary film, which drains into the bottom of the gas cooler. Note that the spatial locations of the aforementioned sprays and films were included in Figure 2 of an earlier published study.7 The hot, wet syngas leaving the gasifier after quenching contains particles entrained in the flow. It is further cooled through heat exchange with water in a vertically mounted gas cooler containing two shell-and-tube heat exchanger modules in series. As a result, water vapor in the gas condenses and, together with the entrained particles, droplets fall down the exchanger tubes into a condensate reservoir used to feed the aforementioned sprays and films.

Plant control is configured to ensure that the level of gas condensate in the pool never falls below a minimum threshold. Any excess, marked as the "condensate return" stream in Figure 1, is returned to the GL dissolver from where it eventually exits the system as GL bound for the pulp mill. Hence, there are no waste streams and the setup reflects an arrangement that may be used in a commercial implementation.

A water-sealed pump is used to keep the GL in circulation in order to avoid sedimentation detrimental to the process. A water flow flushes the bottom of the vessel's external level measurement gauge. Both of these flows empty into the GL dissolver. The gasifier vessel is cooled by atmospheric air while water is used for additional localized cooling of the burner.

Experimental Conditions. The experimental campaign consisted of five operating points (OPs) and values of key process variables are presented in Table 1. OP1 and OP5 represent standard operation denoted by a fuel consumption rate of 21.7 t dry solids (DS) BL/d, a thermal load of ∼5.1 MW and a CH4 concentration of ∼5% in syngas.

The temperature readings presented in Table 1 are influenced by radiation and temperature of both the gas and the ceramic lining. As such, they are not accurate measurements of reactor temperature but rather indications of reactor response to changes in operating parameters. Note that an inverse correlation between reactor temperature and CH4 concentration has previously been established for entrained-flow solid biomass gasification11 and is also present for BLG. The CH4 content in syngas, measured with an online nondispersive infrared sensor (NDIR), was used not only as a marker for reactor temperature but also as an indicator of flame stability. The choice of values was guided by the aim to assess gasifier performance over as large an operating range as possible. This was realized while meeting GL quality criteria and staying within operational constraints on gasifier pressure and load imposed by the downstream DME synthesis unit in production mode.

Each OP remained in place for ∼24 h, which gave a GL turnover factor of 12, based on a hydraulic residence time of ∼1.9 h.12 The length of the operating period not only ensured steady-state conditions at the time of sampling but it also allowed for the discovery of long-term effects and cyclic variations. Data logged by an online refractometer showed a general downward trend in BL solids fraction, which accelerated toward the end of the campaign, as depicted in Figure 2. BL used in the gasifier is imported from the nearby pulp mill and the variation may be seen as an example of fluctuations set in motion by changes to the pulping process. Since the influence of quench tube operation on the process was not among the study’s objectives, variables such as primary flame and spray rates were fixed at 600 kg/h.

Samples of BL at each OP were taken immediately prior to switchover and analyzed following international standards at two independent laboratories: SP Research Institute of Sweden (Botnia, Sweden) and ALS Scandinavia (Uleå, ALS). An elemental analysis on dry basis is provided in Table 2.

Na, K, and S weight fractions were recalculated from measurements made by ALS on a dry basis. The dry solids fraction of the BL fluctuates, depending on operating conditions in the mill and an

<table>
<thead>
<tr>
<th>Operating Point</th>
<th>BL feeding rate (kg/h)</th>
<th>O2/BL (kg/kg)</th>
<th>λ</th>
<th>Syngas composition</th>
<th>Reactor temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP1</td>
<td>1250</td>
<td>0.287</td>
<td>0.491</td>
<td>28.7</td>
<td>1008</td>
</tr>
<tr>
<td>OP2</td>
<td>1250</td>
<td>0.295</td>
<td>0.505</td>
<td>28.7</td>
<td>1036</td>
</tr>
<tr>
<td>OP3</td>
<td>1060</td>
<td>0.284</td>
<td>0.486</td>
<td>28.4</td>
<td>984</td>
</tr>
<tr>
<td>OP4</td>
<td>1060</td>
<td>0.288</td>
<td>0.493</td>
<td>28.1</td>
<td>1001</td>
</tr>
<tr>
<td>OP5</td>
<td>1250</td>
<td>0.285</td>
<td>0.490</td>
<td>28.9</td>
<td>1004</td>
</tr>
</tbody>
</table>

*Ratio of actual oxygen supplied to the stoichiometric requirement for a given mixture. Reactor temperature is dependent on λ, and the measurements presented here are illustrative of the temperature in the proximity of the inner wall close to the center of the reactor.
average of two measured values, adjusted to account for variations recorded by an online refractometer was used in the calculations. The standard enthalpy of formation of BL (ΔHfBL) was obtained by simulation in ASPEN HYSYS with OLI electrolytes (see the Supporting Information), while its standard enthalpy of combustion (ΔHcBL) was determined using bomb calorimetry by SP. BL heat capacity, which is required for the calculation of enthalpy change, was estimated with the help of a generalized empirical relationship developed by Zaman et al.\textsuperscript{13,14} HCO₂⁻ and CO₃²⁻ concentrations in GL were determined by MoRe Research Omskeldvik (MoRe), using potentiometric acid titration.\textsuperscript{15} The suspended solids (“sludge”) fraction was obtained through filtration and subsequent weighing by MoRe. Total carbon (TC) and total organic carbon (TOC) in GL filtrate were determined using a total organic carbon analyzer (Shimadzu, Model TOC-5050), while the total inorganic carbon (TIC) was estimated by subtracting the latter from the former, according to the guidelines in ISO 8425, both of them also determined by MoRe.

S, Na, and K concentrations in gas condensate and GL filtrate were determined using ICP-AES, while TOC and TIC fractions in GL sludge were obtained using coulometry by ALS. Formate (anion of formic acid) concentration in GL filtrate was measured using an ion chromatograph equipped with a conductivity detector by Infuenza AB, Stockholm (Innventia). Syngas samples were collected in gas bags and analyzed with a Varian Model CP-3800 gas chromatograph. The concentrations presented in the study are averages of (normalized) measurements from two separate bags for each OP.

Excluding solids, GL was assumed to comprise of KHS, NaHS, K₂CO₃, Na₂CO₃, KHCO₃, NaHCO₃, Na₂CO₃, and H₂O, while ethanol (C₂H₆O) was chosen as a model compound to represent the large amount of Na present in the fuel. However, SO₂ is used as the final combustion product in HHV calculations of sulfur-containing syngas species. The difference resulting from the use of dissimilar reference states is numerically small; yet, the issue can be circumvented by performing the balance using the enthalpy of formation method (see the Supporting Information). \( \Delta H_f \) of syngas species were computed with reference to standard conditions, defined as \( T_{ref} = 25 \) °C and \( P_{ref} = 1 \) bar with \( \text{CO}_2(g) \), \( \text{H}_2\text{O}(l) \), and \( \text{SO}_2(g) \) as the combustion products of C, H, and S, respectively. The chemical and physical energy content of each stream on enthalpy of combustion basis was computed using eq 1:

\[
\text{CGE}_{\text{Power}} = \sum m_i \Delta H_f^i + m_{j,c} \Delta T
\]

In the above equation, \( m_i \) is the mass flow rate of a given stream, \( \Delta H_f^i \) is the standard enthalpy of combustion for species \( j \), \( \Delta T \) is the specific heat capacity in the relevant temperature interval, and \( \text{CGE}_{\text{Power}} \) is broadly defined as the ratio between the chemical energy in syngas and the chemical energy in the fuel from which it is derived. Three different types of CGEs, calculated based on both HHV BL, and LHV BL are presented in this work: \( \text{CGE}_{\text{fuel}} \), \( \text{CGE}_{\text{fuel,sulfur}} \), and \( \text{CGE}_{\text{fuel,sulfur,gasification}} \). Historically, syngas from biomass was primarily aimed at combustion applications for power generation. \( \text{CGE}_{\text{fuel}} \) takes into account the heating value of all detectable and combustible syngas species such as CH₄ and \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_6 \) \( \text{CGE}_{\text{fuel,sulfur}} \) is calculated from the heating values of CO and \( \text{H}_2 \) and used as a performance measure for biofuel production. As a potential recovery boiler replacement, BLG is required to supply high-quality GL with sulfur in a reduced state for reuse in the pulp recovery cycle. Moreover, COS and H₂S must be removed, and, if possible, recovered from syngas to facilitate biofuel synthesis. Hence, \( \text{CGE}_{\text{fuel,sulfur,gasification}} \) which is seen as a more representative parameter for catalytic upgrading in an integrated Kraft pulping application, is calculated from the sulfur-free heating value of BL and the heating value of fuel-

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**THEORETICAL BASIS**

The high heating value (HHV) is one of the most commonly used measures of a fuel’s chemical energy. In the combustion of BL in a bomb calorimeter, S is oxidized to SO₂ because of the large amount of Na present in the fuel. However, SO₂, is used as the final combustion product in HHV calculations of sulfur-containing syngas species. The difference resulting from the use of dissimilar reference states is numerically small; yet, the issue can be circumvented by performing the balance using the enthalpy of formation method (see the Supporting Information). \( \Delta H_f \) of syngas species were computed with reference to standard conditions, defined as \( T_{ref} = 25 \) °C and \( P_{ref} = 1 \) bar with \( \text{CO}_2(g) \), \( \text{H}_2\text{O}(l) \), and \( \text{SO}_2(g) \) as the combustion products of C, H, and S, respectively. The chemical and physical energy content of each stream on enthalpy of combustion basis was computed using eq 1:

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\text{CGE}_{\text{Power}} = \sum m_i \Delta H_f^i + m_{j,c} \Delta T
\]

In the above equation, \( m_i \) is the mass flow rate of a given stream, \( \Delta H_f^i \) is the standard enthalpy of combustion for species \( j \), \( \Delta T \) is the specific heat capacity in the relevant temperature interval, and \( \text{CGE}_{\text{Power}} \) is broadly defined as the ratio between the chemical energy in syngas and the chemical energy in the fuel from which it is derived. Three different types of CGEs, calculated based on both HHV BL, and LHV BL are presented in this work: \( \text{CGE}_{\text{fuel}} \), \( \text{CGE}_{\text{fuel,sulfur}} \), and \( \text{CGE}_{\text{fuel,sulfur,gasification}} \). Historically, syngas from biomass was primarily aimed at combustion applications for power generation. \( \text{CGE}_{\text{fuel}} \) takes into account the heating value of all detectable and combustible syngas species such as CH₄ and \( \text{C}_2\text{H}_6 \), \( \text{C}_2\text{H}_6 \) \( \text{CGE}_{\text{fuel,sulfur}} \) is calculated from the heating values of CO and \( \text{H}_2 \) and used as a performance measure for biofuel production. As a potential recovery boiler replacement, BLG is required to supply high-quality GL with sulfur in a reduced state for reuse in the pulp recovery cycle. Moreover, COS and H₂S must be removed, and, if possible, recovered from syngas to facilitate biofuel synthesis. Hence, \( \text{CGE}_{\text{fuel,sulfur,gasification}} \) which is seen as a more representative parameter for catalytic upgrading in an integrated Kraft pulping application, is calculated from the sulfur-free heating value of BL and the heating value of fuel-

---

### Table 2. Black Liquor (BL) Elemental Analysis (on a Dry Basis) and Heating Values

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>Average Fraction (%)</th>
<th>Absolute Uncertainty</th>
<th>Lab</th>
<th>Measurement Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>kg/kg BL</td>
<td>27.50\textsuperscript{a}</td>
<td>0.55</td>
<td>SP</td>
<td>element analyzer</td>
</tr>
<tr>
<td>H</td>
<td>kg/kg BL</td>
<td>3.75\textsuperscript{a}</td>
<td>0.23</td>
<td>SP</td>
<td>element analyzer</td>
</tr>
<tr>
<td>N</td>
<td>kg/kg BL</td>
<td>0.07\textsuperscript{a}</td>
<td>0.02</td>
<td>SP</td>
<td>element analyzer</td>
</tr>
<tr>
<td>Cl</td>
<td>kg/kg BL</td>
<td>0.16\textsuperscript{a}</td>
<td>0.02</td>
<td>SP</td>
<td>ion chromatograph</td>
</tr>
<tr>
<td>Na</td>
<td>kg/kg BL</td>
<td>19.5\textsuperscript{a}</td>
<td>3.07\textsuperscript{a}</td>
<td>ALS</td>
<td>ICP-SFMS/AES\textsuperscript{c}</td>
</tr>
<tr>
<td>K</td>
<td>kg/kg BL</td>
<td>3.12\textsuperscript{a}</td>
<td>0.63\textsuperscript{b}</td>
<td>ALS</td>
<td>ICP-SFMS/AES\textsuperscript{c}</td>
</tr>
<tr>
<td>S</td>
<td>kg/kg BL</td>
<td>6.20\textsuperscript{a}</td>
<td>1.24\textsuperscript{b}</td>
<td>ALS</td>
<td>ICP-SFMS/AES\textsuperscript{c}</td>
</tr>
<tr>
<td>O</td>
<td>kg/kg BL</td>
<td>39.55</td>
<td></td>
<td></td>
<td>by difference</td>
</tr>
</tbody>
</table>

\( * \) C, H, N, Cl are averages of measurements at 2 OPs. \( * * \) Na and K, S are calculated using 4 and 5 measurements, respectively, because of the suspicion of measurement error at OPs in the former. 7 Based on information provided by the analysts, recalculated from relative uncertainty where required. 8 On dry basis. 9 On wet basis. 10 Calculated based on ICP-SFMS measurement uncertainty. 11 Three samples were analyzed with ICP-SFMS and two with ICP-AES and the two techniques have measurement uncertainties of 20% and 10%, respectively.
relevant syngas components (CO and H₂). The sulfur-free heating values of BL are computed by subtracting the product of the enthalpy of sulfur oxidization from sulfites to sulfates and BL sulfur mass fraction from the total BL heating values.

**Carbon Conversion.** In applications with only gaseous end-products, carbon conversion efficiency is often defined as the ratio of carbon in syngas to that in the feedstock. In a pulp mill application of BLG, this definition must be modified to account for the need to recover nongaseous total inorganic carbon in GL (GL TIC) for reuse in the pulping process. Note that this conversion efficiency was reported at η = 99.7% in a previous campaign, sulfur reduction efficiency was reported at 100%, within measurement uncertainty limits.11 The approach outlined yielded relatively good charge balance closures, as presented in Table 3. Chloride and formate salts of Na and K were also detected in GL, although their concentrations were miniscule in comparison.

At high pressure, and in the operating temperature range of the gasifier, nearly all Na ends up in GL, as evidenced by the very low Na particle concentrations measured in syngas. The same is assumed to be true of K. TTA change over the campaign is the likely outcome of a combination of factors, mainly varying BL flow rates and compositions. Na and K concentrations at OP3 and OP4 were noticeably lower because the water inflows into GL dissolver did not decrease in proportion to BL load. GL sulfides, calculated on the basis of S concentration, were lower than in GL from sulfite gasification and recovery boilers. In GL, HCO₃⁻ is formed by the absorption of syngas CO₂ and its concentration did not exceed 8% of TTA during the campaign.

A breakdown of both organic and inorganic carbon fractions in the filtrate and the sludge is presented in Table 4. GL carbon fraction is theoretically sensitive to changes in parameters such as CO₂ and CO partial pressures, because of gaseous dissolution, leading to the formation of HCO₃⁻ and HCOO⁻, respectively. In practice, GL TIC matched CO₂ and HCO₃⁻ very well and the deviations did not appear to be systematic in nature.

GL is an alkaline solution rich in Na with a pOH that corresponds to a significant concentration of hydroxide ions. It was thus hypothesized that part of the dissolved carbon may be present as formate ions, because of the reaction of syngas CO with aqueous NaOH described in eq 3 (see the Supporting Information).

\[
\text{NaOH(aq) + CO(g) } = \text{ HCOONa(aq)}
\]

\[
\Delta H_r = -69.46 \text{ kJ/mol}
\]
NaHCOO can be produced industrially at high pressure and temperature around 200 °C and the conditions in the quench satisfy these requirements. A thermodynamic simulation of GL dissolver under experimental conditions, carried out in ASPEN HYSYS using the OLI electrolyte database, confirmed formate formation to be thermodynamically feasible. Ion-chromatographic analysis of GL confirmed formate presence and yielded concentrations between 0.017 and 0.038 mol/L, as shown in Table 3.

A plot of the CO partial pressure against the measured formate molarity (see Figure 3) showed a clear positive correlation between the two. Formate C as a function of CO partial pressure.

Figure 3. Formate ion concentration as a function of CO partial pressure.

Knowledge of GL composition and properties is pertinent to the design and operation of the chemical recovery processes in the pulp mill. It has previously been shown that gasification GL can be handled similarly to the recovery boiler variety for process conditions (30 bar, pH 8.2–8.5). Na and K concentrations in samples, given in Table 5, were relatively low, at ~2% of the corresponding GL.

Table 5. Process Element Concentrations in Gas Condensate

<table>
<thead>
<tr>
<th>OP1</th>
<th>OP2</th>
<th>OP3</th>
<th>OP4</th>
<th>OP5</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.3</td>
<td>8.4</td>
<td>8.3</td>
<td>8.2</td>
</tr>
<tr>
<td>S (mg/L)</td>
<td>3130</td>
<td>2690</td>
<td>3470</td>
<td>4030</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>2050</td>
<td>2050</td>
<td>1970</td>
<td>1940</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>483</td>
<td>509</td>
<td>445</td>
<td>443</td>
</tr>
<tr>
<td>TIC (mg/L)</td>
<td>804</td>
<td>846</td>
<td>849</td>
<td>891</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>628</td>
<td>668</td>
<td>581</td>
<td>367</td>
</tr>
<tr>
<td>(TIC + S)/(Na + K) (mg% basis)</td>
<td>162</td>
<td>151</td>
<td>184</td>
<td>209</td>
</tr>
</tbody>
</table>

Total organic carbon. Total inorganic carbon.

Values. Inorganic carbon was present primarily as HCO₃⁻ at the measured pH. The presence of alkali metals and inorganic carbon can be attributed to particles carried over in syngas that are efficiently stripped out in the gas cooler. As observed in GL, TOC was found primarily as soluble compounds. Sulfur concentrations, which were an order of magnitude higher than those measured in a previous campaign, were well in excess of the values required to close the charge balance. This indicates the presence of some form of uncharged sulfur in gas condensate. However, it is important to note that GL charge balance closures, based on total sulfur concentration measurements, did not deviate by more than 2%, which indicates that the unknown uncharged form of sulfur is transformed to sulfide when the condensate is introduced into the GL dissolver. The identification, transformation, and potential quantification of sulfur-containing species in the GL system is currently the subject of further investigation.

Syngas compositions are presented in Table 6. Cold syngas recorded temperatures of 28–35 °C at the sampling point used in the balances. An increase in ω at constant load (OP2) led to a marked decrease in CH₄ concentration as it was converted to CO and CO₂, as seen from the slight rise in their concentrations. H₂ remained unaffected while H₂S concentration went down by 8%, a value larger than the difference between the two standard-state measurements. This hinted at the presence of a possible minor temperature dependence, also predicted by equilibrium calculations, although at a slightly lower value. C₆H₆ and C₂ hydrocarbons concentrations decreased significantly.

As mentioned above, the reduction efficiency for GL sulfur has previously been shown to be close to 100% for BLG, while typical corresponding values for a recovery boiler GL are 60%–90%. Since sulfate and thiosulfate are not the desired active forms of pulping chemicals, this means the ballast from these substances is reduced or eliminated when gasification is used, hence improving the efficiency. The GL TOC values presented here are somewhat higher than what is typically encountered for recovery boiler GL—1.3–1.8 g/L (Table 4), compared to ~1.0 g/L—but this difference is not believed to necessitate modifications in the pulp mill equipment.

Gas Condensate. Gas condensate from the campaign had a pH of 8.2–8.5. Na and K concentrations in samples, given in Table 5, were relatively low, at ~2% of the corresponding GL.

As observed inGL, TOC was found primarily as soluble compounds. Sulfur concentrations, which were an order of magnitude higher than those measured in a previous campaign, were well in excess of the values required to close the charge balance. This indicates the presence of some form of uncharged sulfur in gas condensate. However, it is important to note that GL charge balance closures, based on total sulfur concentration measurements, did not deviate by more than 2%, which indicates that the unknown uncharged form of sulfur is transformed to sulfide when the condensate is introduced into the GL dissolver. The identification, transformation, and potential quantification of sulfur-containing species in the GL system is currently the subject of further investigation.
Changes in CO and CO$_2$ in response to an increase in residence time (OP3), are likely due to a decrease in reactor temperature, because of lower $\lambda$, as opposed to any inherent residence time effects, as most concentrations remain unchanged and the process, with the exception of CH$_4$, is in equilibrium. Furthermore, since hot syngas comes in contact with both smelt and water in quench and GL dissolver, the measured concentrations are also affected by the magnitude of CO and CO$_2$ absorption in GL.

Gasifier operation at lower pressure (OP4) exhibited a decrease in CH$_4$ and an increase in CO concentrations which may partially be explained by the marginally higher $\lambda$ at this OP, although a weak pressure dependence, more pronounced at lower pressures, has previously been observed. Some pressure dependence is expected since, consistent with Le Chatelier’s principle, a pressure decrease would result in the methane steam reforming reaction shifting to favor CO production at the expense of CH$_4$. However, this effect is likely not fully realized since the reaction does not reach equilibrium.

Finally, a repeat under standard conditions (OP5) resulted in values broadly similar to those recorded at OP1, thereby demonstrating process robustness and repeatability within the operating range. Generally, N$_2$ molar fraction in syngas was demonstrating process robustness and repeatability within the operating range. Generally, N$_2$ molar fraction in syngas was demonstrated to be higher than that in hot gas sampled from the lower part of the reactor near the outlet to the quench tube. Therefore, it is sensitive to variations in quenching parameters such as the ratio of primary spray flow rate to load.

The presence of water vapor in syngas facilitates the release of sulfur in the gas phase and eq 4 has been proposed as a possible reaction pathway.

$$\text{Na}_2\text{S}(s) + \text{H}_2\text{O} (g) + \text{CO}_2 (g) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{S}(g)$$

(COS) concentration in the hot syngas is dictated by equilibrium reactions but it also undergoes hydrolysis to CO$_2$ and H$_2$S during the quenching process. In the past, during experiments with sulfite and kraft liquors, COS values have both shown a greater spread and been considerably higher, on average. Gasifier Mass Balance. Gasifier mass balance closures, presented in Table 7, do not deviate by more than 7%. Flows included in the calculation are shown as solid lines in Figure 1. N$_2$ enters the gasifier at several points. A few of the minor entry streams are not taken into account in the balance, because of the absence of flow measurement devices. The unaccounted N$_2$ amount is estimated to be in the range of 2–3 kg/h (i.e., <0.5% of syngas throughput). Level measurement water flow rate fell below the detection limit of ~60 kg/h at OP4. Nonetheless, a flow was deemed to be present based on operational experience and assigned a value of 30 kg/h, which was subsequently used in balance calculations.

The GL flow rate exhibited short-term fluctuations, which are likely linked to the configuration of a GL control loop and scale buildup. The standard deviations of GL flow measurements, recorded over an hour, were found to lie anywhere between 20 and 60 kg/h, which corresponds to 1%–2% of the flow input. After see-saving at the start of the campaign, the flow rate began to decrease steadily at the commencement of OP2. It appeared to have plunged by 400 kg/h at the point of switchover to OP4, when it increased sharply by 200 kg/h, remaining steady until the end of the campaign. It is not physically possible for the missing volume to have remained in GL dissolver, since that would lead to a significant increase in the level and would be detected immediately. One explanation for the observed trend may lay in measurement errors due to the accumulation of particles in the pipe which continued until partially cleared by an outrushing jet. Thus, the recorded flow was found to be an underestimation and, as a corrective measure, GL flow rates at OP2–OP5 were adjusted upward by 150 kg/h, which is a figure proposed as an average of the missing flow. In summation, both the short-term fluctuations and the unusual long-term trend described above serve to make GL flow the single largest contributor to deviations in mass balance closures.
Process Element Mass Balance. Carbon balance closures are presented in Table 8, and deviation of carbon balance was 5%–6% for all OPs, suggesting the presence of a common error source. Between 85% and 87% of C is carried out in syngas, which is subject to both a mass flow measurement and chromatographic analysis. Also, variations in BL mass flow rates and C fractions have a large influence on the balances; hence, balance closures are vulnerable to measurement errors in these parameters.

An important characteristic of the entrained-flow BLG process is the splitting of inbound sulfur between GL and syngas, which enables the recovery of gaseous sulfur in a separate stream, if desired. Sulfur and sodium balance closures did not deviate by more than 4%, while the corresponding value for potassium was 8%. OP-on-OP change in the closures, illustrated in Figure 5, reveals the presence of a pattern that is common to S, Na, and K. It also implies that the closures for all three elements would be subject to the same error at all five OPs. The source of this error may lie in either measurement of mass flows or element concentrations. The discrepancy of 8% in the balance closure at OP2 in the K balance may potentially stem from an overestimation of its concentration in GL, which happens to be higher than at any other operating point.

The sulfur split, which is defined as the ratio of the amount of sulfur in syngas to the amount of sulfur in BL, ranged between 25% and 28%. The fraction of gaseous sulfur decreased with the gasification temperature, although it increased marginally with the residence time. Note that the split is also influenced by the fraction of sulfur in the chosen fuel, as evidenced by the 70%–73% value seen in a previous campaign running on sulfur-rich sulfite thick liquor.11

Carbon Conversion Efficiency. As seen in Table 9, \%_carbon varied relatively little between the OPs with the exception of OP4—standard gas residence time at lower pressure—when it went down to 96.3%. The dip was the result of a disproportionately high concentration of nonformate GL TOC. Recall that OP4 also yielded the lowest formate fraction.

OPs. The source of this error may lie in either measurement of mass flows or element concentrations. The discrepancy of 8% in the balance closure at OP2 in the K balance may potentially stem from an overestimation of its concentration in GL, which happens to be higher than at any other operating point.

The sulfur split, which is defined as the ratio of the amount of sulfur in syngas to the amount of sulfur in BL, ranged between 25% and 28%. The fraction of gaseous sulfur decreased with the gasification temperature, although it increased marginally with the residence time. Note that the split is also influenced by the fraction of sulfur in the chosen fuel, as evidenced by the 70%–73% value seen in a previous campaign running on sulfur-rich sulfite thick liquor.11

Table 7. Mass Balance over the Gasifier at All OPs

<table>
<thead>
<tr>
<th>In (kg/h)</th>
<th>Out (kg/h)</th>
<th>Closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>black liquor, BL</td>
<td>O2</td>
<td>N2</td>
</tr>
<tr>
<td>OP1</td>
<td>1250.0</td>
<td>359.0</td>
</tr>
<tr>
<td>OP2</td>
<td>1250.0</td>
<td>369.0</td>
</tr>
<tr>
<td>OP3</td>
<td>1060.0</td>
<td>301.0</td>
</tr>
<tr>
<td>OP4</td>
<td>1060.0</td>
<td>305.0</td>
</tr>
<tr>
<td>OP5</td>
<td>1250.0</td>
<td>356.0</td>
</tr>
</tbody>
</table>

*aGL pump sealing water. bLevel measurement water. cSecondary film.

Table 8. Carbon, Sodium, Potassium, and Sulfur Mass Balances for All Operating Points

<table>
<thead>
<tr>
<th>In (kg/h)</th>
<th>Out (kg/h)</th>
<th>Closure</th>
</tr>
</thead>
<tbody>
<tr>
<td>black liquor, BL</td>
<td>green liquor, GL</td>
<td>syngas</td>
</tr>
<tr>
<td>OP1</td>
<td>250.6</td>
<td>52.1</td>
</tr>
<tr>
<td>OP2</td>
<td>250.6</td>
<td>47.4</td>
</tr>
<tr>
<td>OP3</td>
<td>211.7</td>
<td>41.0</td>
</tr>
<tr>
<td>OP4</td>
<td>211.4</td>
<td>41.0</td>
</tr>
<tr>
<td>OP5</td>
<td>246.5</td>
<td>47.7</td>
</tr>
<tr>
<td>OP1</td>
<td>56.2</td>
<td>42.4</td>
</tr>
<tr>
<td>OP2</td>
<td>56.2</td>
<td>44.4</td>
</tr>
<tr>
<td>OP3</td>
<td>47.6</td>
<td>33.6</td>
</tr>
<tr>
<td>OP4</td>
<td>47.6</td>
<td>35.3</td>
</tr>
<tr>
<td>OP5</td>
<td>56.2</td>
<td>40.0</td>
</tr>
</tbody>
</table>

*aSulfur split is defined, on a mass basis, as the amount of sulfur in syngas divided by the amount of sulfur in black liquor.

Figure 5. Sodium, potassium, and sulfur mass balances at all operating points.

Table 9. Carbon Conversion Efficiency and Unconverted Carbon Fraction in Green Liquor

<table>
<thead>
<tr>
<th>OP</th>
<th>%_carbon (%)</th>
<th>nonformate GL TOC/C in GL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP1</td>
<td>98.0</td>
<td>5.8</td>
</tr>
<tr>
<td>OP2</td>
<td>99.0</td>
<td>5.2</td>
</tr>
<tr>
<td>OP3</td>
<td>99.0</td>
<td>5.4</td>
</tr>
<tr>
<td>OP4</td>
<td>98.3</td>
<td>9.0</td>
</tr>
<tr>
<td>OP5</td>
<td>99.2</td>
<td>6.3</td>
</tr>
</tbody>
</table>

*aOn a mass basis.
concentration, likely as a result of the relatively lower partial pressure of CO in syngas. TOC concentration in GL was 1–2 g/L, which amounted to 6%–10% of all the carbon present; 10%–30% of GL TOC came from recirculated gas condensate. The remainder may have originated in surface buildup or fallen down with the smelt itself; further characterization of GL TOC could help pinpoint the exact source. These concentrations are comparable to a TOC value of ~1 g/L in recovery boiler GL from the Smurfit Kappa Kraftliner Piteå (SKKP) mill, which was measured in association with the sampling campaign. Lower concentrations have been measured in past campaigns at the plant. Note that, in the present plant setup, gas condensate is recycled and used as dissolving fluid for GL production, which was not the case previously. It is worth bearing in mind that a change of 0.1% in T°fi of CO in syngas or as sensible heat carried by gas condensate, which amounted to 23%–27% of the total heat input. Furthermore, 13%–15% is carried away by GL flow primarily as sensible heat, chemical energy in GL TOC accounts for only 5%–8% of GL energy flow. Note that C₂H₄O, which is the model compound used to represent GL TOC, has a relatively high heating value and the actual value may be slightly lower or higher. In a commercial implementation, the sensible heat carried by GL and cooling flows could be recovered and utilized, typically to partially fulfill pulp mill process heat requirements. Part of the discrepancy in closures is due to diffuse heat losses, which are not explicitly included in the balance. Another contributory factor, in particular at OP3, is the drop in GL mass flow rate, as noted earlier in the mass balance discussion.

### Cold Gas Efficiencies

BLG CGEs, given in Table 11, are comparatively lower than those for entrained-flow biomass or coal gasification, because of high moisture and inorganic content. The difference is further compounded by the need to use part of the energy to regenerate vital pulping chemicals. In addition, CGE is negatively influenced by the gasifier’s small scale, in comparison to a commercial plant. The BL used in this campaign yielded markedly lower carbon concentrations with a higher O/C ratio than the composition reported in a previous study. Accordingly, the λ values were significantly higher, which led to lower CGEs across the board. As has been observed previously, CGE_fuel values decreased at higher λ (OP2) while CGE_fuel values increased, partially

<table>
<thead>
<tr>
<th>Table 11. Process Cold Gas Efficiencies and Syngas Heating Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>OP1</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td><strong>On HHV Basis</strong></td>
</tr>
<tr>
<td>syngas HHV_fuel (MJ/Nm³)</td>
</tr>
<tr>
<td>syngas HHV_power (MJ/Nm³)</td>
</tr>
<tr>
<td>CGE_{fuel} (%)</td>
</tr>
<tr>
<td>CGE_{power} (%)</td>
</tr>
<tr>
<td>CGE_{total} (%)</td>
</tr>
<tr>
<td><strong>On LHV Basis</strong></td>
</tr>
<tr>
<td>syngas LHV_fuel (MJ/Nm³)</td>
</tr>
<tr>
<td>syngas LHV_power (MJ/Nm³)</td>
</tr>
<tr>
<td>syngas LHV_power (~N)</td>
</tr>
<tr>
<td>CGE_{fuel} (%)</td>
</tr>
<tr>
<td>CGE_{power} (%)</td>
</tr>
<tr>
<td>CGE_{total} (%)</td>
</tr>
</tbody>
</table>

*Taken into account the HHV of all syngas components. *CO and H₂ only. *CO and H₂ only on a sulfur-free basis.

---

Table 10. Gasifier Energy Balance on Standard Enthalpy of Combustion (ΔH°*) Basis

<table>
<thead>
<tr>
<th>OP</th>
<th>OP1</th>
<th>OP2</th>
<th>OP3</th>
<th>OP4</th>
<th>OP5</th>
</tr>
</thead>
<tbody>
<tr>
<td>In (kW)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>black liquor</td>
<td>sensible</td>
<td>97.0</td>
<td>97.0</td>
<td>82.3</td>
<td>82.3</td>
</tr>
<tr>
<td></td>
<td>chemical</td>
<td>3070.1</td>
<td>3070.4</td>
<td>2593.3</td>
<td>2589.8</td>
</tr>
<tr>
<td>O₂</td>
<td>sensible</td>
<td>2.4</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>N₂</td>
<td>sensible</td>
<td>−0.1</td>
<td>−0.1</td>
<td>−0.1</td>
<td>−0.1</td>
</tr>
<tr>
<td>GL pump sealing water</td>
<td>sensible</td>
<td>21.5</td>
<td>22.4</td>
<td>21.5</td>
<td>24.4</td>
</tr>
<tr>
<td>level measurement water</td>
<td>sensible</td>
<td>6.9</td>
<td>8.5</td>
<td>9.4</td>
<td>1.7</td>
</tr>
<tr>
<td>secondary film</td>
<td>sensible</td>
<td>−11.9</td>
<td>−12.8</td>
<td>−13.1</td>
<td>−14.7</td>
</tr>
<tr>
<td>Out (kW)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>green liquor</td>
<td>sensible</td>
<td>454.9</td>
<td>413.5</td>
<td>390.8</td>
<td>412.2</td>
</tr>
<tr>
<td></td>
<td>chemical</td>
<td>344.8</td>
<td>346.2</td>
<td>227.4</td>
<td>348.3</td>
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<tr>
<td>syngas</td>
<td>chemical</td>
<td>1.4</td>
<td>1.0</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>vessel cooling</td>
<td></td>
<td>1535.5</td>
<td>1511.4</td>
<td>1333.4</td>
<td>1303.4</td>
</tr>
<tr>
<td>support ring cooling</td>
<td></td>
<td>108.9</td>
<td>113.8</td>
<td>71.8</td>
<td>75.3</td>
</tr>
<tr>
<td>burner cooling</td>
<td></td>
<td>15.4</td>
<td>13.6</td>
<td>19.0</td>
<td>13.5</td>
</tr>
<tr>
<td>syngas</td>
<td></td>
<td>626.9</td>
<td>685.0</td>
<td>492.4</td>
<td>502.3</td>
</tr>
<tr>
<td>difference (Out−In) (%)</td>
<td>48.0</td>
<td>−53.5</td>
<td>−110.6</td>
<td>20.0</td>
<td>−63.8</td>
</tr>
<tr>
<td>closures (Out/In) (%)</td>
<td>98.5</td>
<td>98.3</td>
<td>98.9</td>
<td>100.7</td>
<td>98.0</td>
</tr>
</tbody>
</table>

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Energy & Fuels
because of the conversion of energy-rich CH₄ to CO and CO₂.

By definition, CGEₙ₅₀ is correlated to the concentrations of H₂
and CO in syngas. Although the former did not appear to be
significantly influenced by process changes, more of the latter
was produced at OP₂–OP₄, which is reflected in the CGEₙ₅₀
values. Thus, running the gasifier at a higher λ operating
point would appear to be beneficial to fuel production. It is
expected that CGEₙ₅₀ would reach an optimum at tempera-
tures in the vicinity of those measured at OP₂. Substantially
hotter operation is likely to experience a decrease, because of an
increase in the amount of CO₂ produced, which would outstrip
the dwindling CO produced from CH₄ conversion. Moreover,
operation at elevated temperatures can increase thermal stresses
in the ceramic material used to line the reactor and thus
adversely affect its service life. Hence, the choice of gasifier
operating temperature in a commercial facility would involve
balancing gains in CGEₙ₅₀ against lining material cost, specific
service life degradation, and increased oxygen usage.

Variations in H₂S concentration were relatively small
between OPs and COS was present in miniscule amounts. In
total, sulfur-containing species in syngas account for 2.3%–
2.5% of the BL HHV. Sulfur-free BL HHV is susceptible to
variations in sulfide concentration between OPs, which, in turn,
influence the CGEₙ₅₀ values. Note that the energy
consumed in sulfide reduction accounts for 5%–7% of BL
HHV. This energy should be included in the de facto energy
efficiency calculation of the BLG process if the production of
sulfur in reduced form is considered to be an essential
downstream use in a pulping biorefinery implementation.

It has been shown previously that thermodynamic equili-
brium modeling predicts the syngas composition well if the
minor components CH₄ and H₂S are prescribed. In contrast to
equilibrium predictions, in reality, the endothermic CH₄
reforming that yields CO and H₂ occurs to a lesser extent.
Based on syngas compositions in Table 6, this results in lower
CGEₙ₅₀, by ~2%–6% or 1%–3%, on an absolute basis and a
relative basis, respectively, in comparison to the theoretical
values. CH₄ reforming has a smaller influence on CGEₚ₉₅₀
values, which are calculated using both CH₄ and CO/H₂.
Carbon conversion, at 99% (Table 9), represents another
important deviation from equilibrium, which predicts a 100% conversion,
thereby resulting in CGEs that are somewhat lower than the theoretical values. However, overall, the experimental results presented in this study are much closer to theoretical values from thermodynamic equilibrium than is the case for many other gasification processes, such as fluidized-
bed biomass gasification.

**CONCLUSION**

Syngas produced in the campaign was virtually tar-free with
typical hydrocarbon concentrations in the single-digit ppm
range, with the exception of CH₃OH, which was present at 16–
127 ppm. Fractions of main gas components, H₂ in particular,
appear to be largely unaffected by operating point changes.
CH₄ and C₂H₄ concentrations not only tallied each other but,
by falling significantly at higher λ, also showed the sharpest
relative variation among syngas components.

Element balances closed reasonably well. They were found to
be sensitive to fluctuations in GL flow, which is the largest and
the most unsteady parameter in the process. Approximately
85%–87% of the feedstock carbon left the gasifier in syngas,
whereas the remainder ended up primarily in the form of
inorganic carbonates (1.33–1.65 mol/L) and bicarbonates
(0.1–0.26 mol/L) in GL. All inbound Na and K ended up in
GL, while the sulfur split between GL and syngas did not show
any systematic variation.

The absorption of CO in GL was confirmed as a potential
pathway for formate formation, and thus a source of GL TOC,
in thermodynamic equilibrium simulation of GL dissolver.
Formate molarity in GL seemed to be correlated to the CO
partial pressure. It is worth noting that GL organic fraction
amounted to no more than 1%–2% of the total carbon input,
10%–28% of which was found to be present as formate ions.
η₈₅₀ was 98.3%–99.2% and, because of the high carbon
conversion efficiencies, only 1.3%–2.3% of the chemical energy
input was lost in the form of GL TOC. Hence, the contribution
of CO dissolution to losses in both conversion and energy
efficiencies may be seen as relatively minor. Variations in η₈₅₀
between operating points appeared to be independent of changes in λ, pressure, or residence time within the gasifier’s
operating envelope.

The analysis of gas condensate samples indicates the
presence of unknown uncharged forms of sulfur, which are
transformed to sulfide. The fact that there are no obvious
indications of these unknown species in GL samples indicates a
transformation upon mixing condensate with GL in the GL
dissolver.

The results from this study show the stability of the plant
under varying operating conditions. The performance of
detailed element and mass balances has helped identify and
specify facets of BLG that require further research, namely,
characterization of sulfur species and dissolved organic carbon
compounds present in the gas condensate and GL systems. A
more-complete characterization of GL TOC is contingent upon
the development of analytical methods that are able to identify
low-molecular-weight soluble organic compounds. The data
obtained in the study may be further used for techno-economic
analysis, system design, and process benchmarking. Variations
in BL solids fraction and composition do occur and require
minor operational adjustments, leading to small variations in λ
and, consequently, CH₄ concentration in syngas. However, the
degree of their influence on η₈₅₀ in particular appears to be
limited. On the other hand, quantification of the sensitivity of
CGEs, if any, to these variations may merit further
investigation.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the
ACS Publications website at DOI: 10.1021/acs.energyfuels.6b00349.

Enthalpy of formation of black liquor (S1), formate
formation in GL (S2), and energy balance on standard
enthalpy of formation basis (S3) (PDF)

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Notes

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REFERENCES

Supporting Information

Performance of an entrained-flow black liquor gasifier

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**S1. Enthalpy of formation of Black Liquor**

An accurate determination of black liquor’s enthalpy of formation is important for performance of gasifier energy balance on enthalpy of formation basis. However, there is no straightforward approach to calculating it owing to the difficulty in identifying the distribution of the inorganic and organic compounds in a given black liquor mixture. Therefore, a workaround is to determine the higher heating value as well as enthalpy of formation of the final mixture of the combusted compounds in the calorimetric bomb. This may be done by applying Hess’s law and the following equation:

\[
\text{HOF}_{\text{Black Liquor}} = \text{HOF}_{\text{Combustion Products}} - \text{HHV} \quad (S1)
\]

The potential issue with this equation lies in determination of the true composition of the final mixture in the calorimetric bomb after combustion. To determine this, an advanced calculation module (ASPEN HYSYS with OLI electrolytes) was used, containing an extensive database of electrolytes. This was done to ensure that the concentration of the inorganic compounds in the final liquid solution was included in the calculation.

![Figure S1: ASPEN HYSYS (OLI database) process flow diagram.](image)
The calculation was performed on the basis of unit mass of black liquor. This was further compared with the calculation by assuming arbitrary distribution of the compounds produced after combustion of black liquor. Figure S1 shows the configuration used for ASPEN HYSYS using the properties from OLI electrolytes. The input stream was created by distributing the final products in a bomb calorimeter arbitrarily. It was then allowed to dissociate in the aqueous phase according to the OLI electrolyte. The basis for the calculation was combusted 1000 kg dry black liquor (≈1371.7 kg wet). The enthalpy of formation of the combusted streams of both dry and wet black liquor can be seen in Figure S1. Enthalpy of formation of black liquor can therefore be determined by using Eq. (S1). For example, HOF of dry black liquor = (-20.04-(-12.13)) MJ/kg = -7.91 MJ/kg.

For arbitrary distribution of the combusted compounds, the streams were created with the same distribution used as feed stream for the ASPEN HYSYS OLI simulation. The enthalpies of formation of the combustion products were taken from the NIST (National Institute of Science and Technology) web book. The comparison was done on both dry and wet mass of black liquor respectively in Table S1.

**Table S1: Table of combustion product distribution and calculated HOF values (arbitrary combustion product distribution):**

<table>
<thead>
<tr>
<th>BL. Dry basis, 1000 kg</th>
<th>BL. Wet basis, 1371.74 Kg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Combust. Prod.</strong></td>
<td><strong>Distribution (kg)</strong></td>
</tr>
<tr>
<td>H₂O</td>
<td>337.8</td>
</tr>
<tr>
<td>CO₂</td>
<td>841.7225</td>
</tr>
<tr>
<td>N₂</td>
<td>0.650302</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.044067</td>
</tr>
<tr>
<td>KCl</td>
<td>0.651874</td>
</tr>
</tbody>
</table>
The results were not significantly different from the values generated by OLI electrolytes (0.26 MJ/kg on wet basis). However, compared to the nominal plant capacity (3 MW thermal), it will introduce an error of approximate 2.53% to the calculation if the values from hand calculation were used:

\[
\text{Possible Calculation Error (\%)} = \frac{1}{3} \left(0.26 \times \frac{1050}{3600}\right) \times 100 = 2.53\%
\]

Hence, in this paper, the value obtained from the OLI electrolyte was used to perform energy balance on enthalpy of formation basis.

**S2. Formate formation in Green Liquor**

One of the features of pressurized black liquor gasification is the organic carbon compounds trapped in green liquor. The most significant impact of this phenomenon is on fuel conversion. When green liquor was analyzed for total inorganic and organic carbon, it was found that organic carbon content was much higher than expected. In the beginning, it was assumed to be made up of low molecular weight compounds of unconverted carbon, dissolved in the solution, thereby affecting the total conversion of black liquor. To assess the gasification potential of black liquor,
it is of great importance to identify the true carbon containing compounds in GL. This, in turn, allows the determination of the source, i.e. unconverted carbon in smelt from the reactor or compounds from syngas. Out of several possibilities, it was speculated that carbon monoxide might be present in the alkaline green liquor solution as formate. This was verified by determining the presence of formate ions by analytical measurement. However, the question remains – how was it formed?

One probable explanation could be the reaction of NaOH and CO under severe conditions (high pressure and temperature) to form HCOONa in green liquor by an exothermic reaction –

\[ \text{NaOH (aq)} + \text{CO (g)} = \text{HCOONa (aq)} \quad \Delta H^{\circ} = -69.46 \text{ kJ/mol} \ [1] \]

Evidently, this reaction is favored at high pressure owing to the decrease in the number of molecules and also reduction of volume due to the production of salt in the liquid solution from (CO) gas (Le Châtelier's principle). Moreover, this is basically the commercial method for producing sodium formate based on a few patents [2,3]. The first patent [2] developed for the Solvay Process Company states that the reaction of NaOH and CO should be at around 200 °C and high pressure. This was further clarified by another patent [3] for continuous production of sodium formate (assigned to Mitsubishi Gas Chemical CO. Ltd.). This patent claims that the optimum condition for producing sodium formate would be around 220 °C and between 12 – 30 bar.

Furthermore, to obtain a representative theoretical basis of this process, thermodynamic simulation was performed in ASPEN HYSYS using the OLI electrolyte database. As there is not enough thermodynamic (i.e. Gibb’s free energy) and physical data present for all the components in the database of the software, an indirect approach was adopted to draw any conclusion. Two
streams were mixed in a mixer block in ASPEN HYSYS – one containing all the electrolytes in aqueous solution and the other containing only gas. The pressure and temperature were kept as the same as the actual case in the green liquor tank (30 bar and 200 °C). Figure S2 shows the configuration used for this simulation. The compounds used in the simulation were – NaOH, H₂O, HCOONa, CO and N₂. CO and N₂ were fed as a separate gas stream and mixed with a 0.1 molar NaOH solution (4 kg NaOH). To keep the system temperature constant at 200 °C after mixing of the gas and liquid stream, a heater was used.

**Figure S2: Simulation and calculation of Gibbs free energy of the system by difference**

The Gibb’s free energy was calculated from the enthalpy of formation, temperature and entropy of the mixed stream. The same calculation was performed by creating a separate stream by replacing the NaOH completely with HCOONa and reducing the CO content by the same amount. After that, both the streams were compared on the basis of Gibb’s free energy. It was found that the one containing formate ions (HCOONa) had lower Gibbs free energy than the one
with NaOH resulting in an overall negative Gibbs free energy for formate production ($-1.14 \times 10^5$ kJ/kmol of NaOH).

Therefore, based on the thermodynamic simulation, the preliminary hypothesis for the formation of formate ions in the green liquor was verified. From the analytical measurements, it appeared to account for up to 0.45 % of carbon in syngas.

**S3. Energy balance on standard enthalpy of formation basis**

Standard enthalpy of formation ($\Delta_f H^\circ$) is defined as the change in enthalpy when one mole of a substance is formed from its constituent elements in their standard states (at 25°C and 1 bar). It is difficult to compute directly in case of BL due to a large number of unknown organic and inorganic constituents which may vary from sample to sample. A workaround involves the calculation of $\Delta_f H^\circ$ of the product mixture in the calorimetric bomb by applying Hess’ law as shown in eq 1.

$$\Delta_f H^\circ_{\text{Black Liquor}} = \sum \Delta_f H^\circ_{\text{Combustion products}} - HHV_{BL} \tag{2}$$

In this equation, $\Delta_f H^\circ_{\text{Black Liquor}}$ is the standard enthalpy of formation of black liquor, $HHV_{BL}$ the higher heating value of black liquor and $\sum \Delta_f H^\circ_{\text{Combustion products}}$ is the sum of the standard enthalpies of formation of the combustion products. Hence, in this work, energy balances are performed using both the experimentally determined BL HHV as well as the more fundamental enthalpy of formation method.

The thermal load of each stream on enthalpy of formation basis was computed using eq. 1.

$$\sum \dot{m}_i x_j \Delta_f H^\circ_j + \dot{m}_i c_{pj} \Delta T \tag{3}$$

In the above equation, $\dot{m}_i$ is the mass flow rate of a given stream, $x_j$ is the mass fraction of species $j$ in that stream, $\Delta_f H^\circ_j$ is the standard enthalpy of combustion for species $j$, $c_{pj}$ is the
specific heat capacity in the relevant temperature interval and $\Delta T$ is the difference between $T_{\text{measured}}$ and $T_{\text{ref}}$.

Table S2: Gasifier energy balance on standard enthalpy of formation basis

<table>
<thead>
<tr>
<th>In (kW)</th>
<th>OP1</th>
<th>OP2</th>
<th>OP3</th>
<th>OP4</th>
<th>OP5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black liquor</td>
<td>-3499.9</td>
<td>-3499.8</td>
<td>-2974.5</td>
<td>-2980.0</td>
<td>-3528.0</td>
</tr>
<tr>
<td>$O_2$</td>
<td>2.4</td>
<td>2.5</td>
<td>2.0</td>
<td>2.0</td>
<td>2.4</td>
</tr>
<tr>
<td>$N_2$</td>
<td>-0.1</td>
<td>-0.1</td>
<td>-0.1</td>
<td>-0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>GL Pump Sealing Water</td>
<td>-1207.9</td>
<td>-1247.4</td>
<td>-1187.2</td>
<td>-1387.7</td>
<td>-1259.6</td>
</tr>
<tr>
<td>Level Measurement Water</td>
<td>-519.6</td>
<td>-641.9</td>
<td>-692.8</td>
<td>-130.6</td>
<td>-774.5</td>
</tr>
<tr>
<td>Secondary Film</td>
<td>-4416.0</td>
<td>-4416.9</td>
<td>-4417.2</td>
<td>-5167.2</td>
<td>-4415.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Out (kW)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Green liquor</td>
<td>-9561.1</td>
<td>-9490.0</td>
<td>-9036.8</td>
<td>-9893.3</td>
<td>-9737.4</td>
</tr>
<tr>
<td>Syngas</td>
<td>-1340.6</td>
<td>-1376.0</td>
<td>-1135.8</td>
<td>-1146.0</td>
<td>-1340.4</td>
</tr>
<tr>
<td>Vessel cooling</td>
<td>50.1</td>
<td>50.0</td>
<td>47.4</td>
<td>50.6</td>
<td>52.3</td>
</tr>
<tr>
<td>Support ring cooling</td>
<td>108.9</td>
<td>113.8</td>
<td>71.8</td>
<td>75.3</td>
<td>105.8</td>
</tr>
<tr>
<td>Burner cooling</td>
<td>15.4</td>
<td>13.5</td>
<td>19.0</td>
<td>11.5</td>
<td>12.8</td>
</tr>
<tr>
<td>Syngas cooling</td>
<td>626.9</td>
<td>685.0</td>
<td>492.4</td>
<td>502.3</td>
<td>664.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Total Difference (Out-In) kW</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Closure Out/In (%)</td>
<td>105.4</td>
<td>103.2</td>
<td>104.0</td>
<td>108.8</td>
<td>103.9</td>
</tr>
</tbody>
</table>

The net enthalpies of formation of all substances in the balance are negative; their values are preceded by a negative sign to indicate this in Table S2. By definition the enthalpy of formation of elements in their standard state is zero, thus, $O_2$, $N_2$ and air only have a sensible energy component. Net thermal load of each stream was determined by adding or subtracting the
sensible energy component from the enthalpy of formation component depending on whether the stream temperatures were above or below $T_{\text{ref}}$. Uncertainties and inaccuracies in GL mass flow rate measurement have a proportionally greater influence on discrepancies in mass balance on $\Delta H^\circ$ basis. This is because, in the enthalpy of formation method, most of the energy available is accounted for in the formation of water which makes up the majority of GL. Performing energy balances on enthalpy of combustion basis was found to be the more robust approach since due to a lower sensitivity to large fluctuations in GL flow.

References


Paper II

A Study of Black Liquor and Pyrolysis Oil Co-gasification in Pilot-Scale
A study of black liquor and pyrolysis oil co-gasification in pilot-scale

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Abstract
The effect of blend ratio and reactor temperature on the gasification characteristics of pyrolysis oil (PO) and black liquor (BL) blends with up to 20 wt% PO was studied in a pilot-scale entrained-flow gasifier. In addition to unblended BL, three blends with PO/BL ratios of 10/90, 15/85 and 20/80 wt% were gasified at a constant load of 2.75 MWth. The 15/85 PO/BL blend was used to investigate the effect of temperature in the range 1000-1100°C.

The decrease in fuel inorganic content with increasing PO fraction resulted in more dilute green liquor (GL) and a greater portion of the feedstock carbon ended up in syngas as CO. As a consequence, the cold gas efficiency increased by about 5%-units. Carbon conversion was in the range 98.8-99.5% and did not vary systematically with either fuel composition or temperature. Although the measured reactor temperatures increased slightly with increasing PO fraction, both unblended BL and the 15% PO blend exhibited largely similar behavior in response to temperature variations.

The results from this study show that blending BL with the more energy-rich PO can increase the cold gas efficiency and improve the process carbon distribution without adversely affecting either carbon conversion or the general process performance.

Keywords
Black liquor; pyrolysis oil; gasification; pilot-scale; co-gasification; thermochemical conversion.
1 Introduction

The development and large-scale deployment of cost-effective, liquid biofuels has been identified as a key to success in the march towards the de-fossilization of the transport sector. In the past decade, biomass gasification is one of the pathways for biofuel production that has made several large strides towards commercialization.\cite{1,2}

Originally developed by Chemrec AB, the pressurized entrained-flow (EF) black liquor gasification (BLG) technology has now been demonstrated for 28 000 hours at the 3 MW\textsubscript{th} LTU Green Fuels pilot plant in Piteå, Sweden. Since its completion in 2005, the plant has been the site of several investigations into the gasification characteristics of black liquor (BL), which is a by-product of the pulping process.\cite{3−8} The catalytic effect of BL alkali content ensures the production of a low-methane, tar- and soot-free syngas at residence times in the order of seconds, and at temperatures around 1000-1050°C.\cite{3} Meanwhile, the pulping chemicals are recovered for reuse in a manner similar to that in a pulp mill with a recovery boiler.

The presence of the catalytic effect\cite{9} as well as the existent supply chains in the pulp and paper industry\cite{10} make BL uniquely suited to the production of syngas for subsequent biofuel production.\cite{11} However, it is a hard to transport, energy-poor fuel whose availability is tied to pulp production at a given location. Blending BL with pyrolysis oil (PO), a similar yet more energy-rich fuel with none of the aforementioned disadvantages, offers a means of improving operational flexibility and increasing biofuel yield.\cite{12} A techno-economic evaluation of PO/BL co-gasification showed that the use of a 25% PO blend could increase methanol production by 88% and energy efficiency by 4% compared to unblended BL.\cite{13}

The blending of BL with PO leads to a net decrease in fuel alkali content. It was seen in a study of coal-char gasification\cite{14} that above a alkali/C atomic ratio \(\approx 0.1\), the catalytic activity of alkali reaches a saturation level. A similar effect may also be expected to exist for biomass. A few studies\cite{15,16} observed a linear increase in the gasification reactivity of biomass chars with increasing alkali content (alkali/C ratio <0.1). In another study\cite{9}, the opposite approach was adopted by reducing BL alkali content through incremental addition of PO. The char and droplet conversion rates of the resulting blends with up to 30% PO were found to be similar to those of unblended BL. Hence, the addition of PO did not at all affect the gasification reactivity of the BL/PO blends, thereby supporting the plateaued catalytic activity. However, none of these lab-scale (<900°C and atmospheric) studies account for the high (flame) temperature as well as heating rate, and the resulting significant alkali release that is encountered in actual gasifiers. Moreover, syngas compositions and process energy efficiencies at
different PO/BL blends ratios have only been estimated by simulation and, therefore, require validation, further study and detailed experimental quantification in a more industrially-representative scale.

The main aim of this study was to investigate, quantify, and assess the effect of PO/BL blend ratio on syngas composition, sulfur distribution, carbon conversion, smelt composition and cold gas efficiency in pilot-scale under steady-state operation. A secondary aim was to study and compare the effect of reactor temperature on the gasification characteristics of a 15/85 PO/BL blend with those of unblended BL.

2 Material and methods

The BLG process consists of a pressurized, oxygen-blown EF gasifier with a refractory-lined reactor vessel, which converts sulfur- and alkali-rich BL, and blends thereof, into syngas and recoverable smelt. An overview of the major process components and media streams is shown in Figure 1. A detailed schematic of all the media streams included in the mass and energy balances is provided in Appendix A1 in the Supplementary Information.

Before it is sent to the synthesis plant, syngas is cooled to around 30°C in two stages: initially in a direct quench, and subsequently indirectly in a vertical gas cooler. In the process, it is stripped of particulates which are eventually recirculated back, together with condensed syngas tars, to a pool of liquid at the bottom of the gasifier that also contains the dissolved smelt in an aqueous solution named green liquor (GL). Further details can be found in an earlier parametric study[5] as well in a recently published performance assessment of black liquor gasification.[7]

The BL used in this study was taken from the neighboring Smurfit Kappa Kraftliner Piteå (SKKP) pulp mill, while the PO was produced at the Fortum bio-oil plant in Joensuu, Finland. In order to store and feed PO, a continuously-stirred 2.2m³ day-tank and two pumps were installed in the vicinity of the gasifier. The risk of lignin precipitation, which may occur do to the formation of pH gradients was minimized by mounting a pressurized mixer before the gasifier, thereby ensuring comprehensive physical mixing of BL and PO. The co-gasification of the PO/BL blends did not require any modification to either the design of the burner nozzle or the operation of the existing gasifier feeding system.

2.1 Experimental conditions

During the experimental run, the gasifier was continuously operated on BL and three PO/BL blends at eight different settings. One of the BL settings was repeated in triplicate and fuel feed data for the resulting individual
operating points (OPs) is presented in Table 1. In total, more than 130 tons of kraft BL and ~5 tons of PO were
gasified over five days. In the present study, “standard operating conditions” denote a thermal load of 2.75 MW
and a CH₄ content of 1.2 mol% in syngas, which was obtained by adjusting the oxygen flow to the reactor. This
can be compared to a typical operating load of ~3.1 MWth on BL. A slightly reduced thermal load was used to
maximize operational stability and the potential for quantifying the effects of the investigated parameters.

The effect of blending ratio was investigated by gasifying BL and blends with PO/BL ratios of 10/90, 15/85 and
20/80 on a mass basis at standard operating conditions. The effect of reactor temperature was studied by
operating the gasifier on a 15% PO blend at three different temperature settings denoted by syngas CH₄ fractions
of 0.5%, 1.2% and 2.1% and labeled “hot”, “standard” and “cold”, respectively. Although the day-tank capacity
placed an upper limit on the duration of co-gasification experiments, all the OPs were in place for at least 6
hours, which is three times the hydraulic residence time of GL. Due to the partial dissociation of organic acids
found in PO, a temperature rise of 5-10°C was observed in the mixer. However, the temperature of the fuel feed
to the reactor was maintained between 140-145°C by regulating the temperature of the BL to the mixer. A
detailed breakdown of BL and PO compositions is presented in Table 2. In comparison with BL, PO contains
significantly more carbon, marginally more oxygen, and virtually no ash. Meanwhile, a substantial fraction of
the oxygen and carbon in BL is present as inorganic carbonates of sodium and potassium. Accordingly, PO has a
considerably higher heating value than BL. Hence, at constant thermal load, the total fuel feed rate decreased
with increasing PO fraction. The 10%, 15% and 20% PO blends had PO/BL ratios of 17/83, 25/75 and 32/68,
respectively on an energy basis.

A number of calibrations were performed to improve flow measurement accuracy and they are discussed in more
detail in section A1 of the Supplementary Information. Media samples from the study were analyzed at a number
of laboratories, which are collated in Tables 2 and 3. Note that the general procedure use for the calculation of
the energy balances was detailed recently.[7] The standard conditions used as the reference points for the
calculation of BL standard enthalpy of combustion were defined as $T_{ref} = 25°C$ and $P_{ref} = 1$ bar, with $K_2CO_3 (s)$,
Na₂CO₃ (s), CO₂ (g), H₂O (l) and Na₂SO₄ (s) as the stoichiometric combustion products. The total titrable alkali
(TTA) was calculated by summing the sulfide, carbonate and bicarbonate concentrations.

2.2 Characteristic ratios
Similarly to coal, the difference in heating values between biomasses with low ash content has been correlated to
differences in O/C and H/C ratios.\[17\] Although both of these ratios offer a useful means of fuel classification,
they do not explicitly take into account the effect of variations in inorganic content on fuel properties such as
heating value. Thus, for alkali-rich fuels like BL, a parameter such as alkali/C ratio, which decreases with
increasing PO fraction, provides a more representative means of characterization. In the present work, the blends
are classified in terms of their molar alkali-to-carbon ratio for quantitative comparisons.

The reactor temperature has been shown to be a nearly linear function of $\lambda$ in entrained-flow gasification at
steady-state conditions.\[18\] By definition, $\lambda$ does not take into account variations in fuel oxygen content.\[19\]
This can conceal the role played by the oxygen native to a fuel which, in most instances, is also available to the
gasification reactions taking place in the reactor. In this study, the relative oxygen content (ROC) is used as a
fuel-independent measure of the total oxygen available in the reactor. ROC, which has been used previously in
studies on biomass gasification,\[20\] is defined as follows:

\[
ROC = \frac{O_2_{\text{additional}} + O_2_{\text{fuel}}}{O_2_{\text{stoich}} + O_2_{\text{fuel}}} \quad (1)\[19\]
\]

In eq 1, $O_2_{\text{additional}}$ stands for gaseous oxygen added to the gasifier, $O_2_{\text{fuel}}$ represents the fuel oxygen content, and
$O_2_{\text{stoich}}$ denotes the gaseous oxygen required for stoichiometric combustion. The $\lambda$ values of all OPs are plotted
as a function of ROC in Figure 2. ROC and $\lambda$ have a unique relation for each distinct fuel composition, as
exemplified by the lines for BL and the 15% PO blend. The position of each line is determined by both the fuel
oxygen content and the stoichiometric oxygen demand. For each fuel composition, the position along the $\lambda$-ROC
line is set by the amount of added gaseous oxygen, with “hot” OPs to the top-right. Although Figure 2 is based
on a constant PO and BL solids composition, (Table 2) it does incorporate the effect of variations in BL solids
fraction, which are chiefly responsible for any deviations from the straight line. The solids fraction in BL from
the SKKP mill has been shown to vary cyclically,\[7\] and it went down by nearly 2% over the course of the
present experimental run. On Figure 2, the “standard” OP lies much closer to the “cold” OP than to the “hot” OP
for the 15% PO blend. Since additional oxygen requirement is determined by controlling syngas methane
content, the amount needed to reach the set value of 1.2% was less than expected. One potential cause may be an
uncontrolled variation in BL solids composition, which led to a small decrease in BL carbon content, and thus
the oxygen demand.
In view of the likely applications, BLG energy efficiency was quantified using three different parameters on a LHV basis. CGEPower takes into account the heating value of all syngas components. CGEFuel only considers CO and H\(_2\): the two most important components for chemical synthesis, while CGEFuel+S-free is calculated on a sulfur-free basis to capture the importance of sulfur recovery to the pulp mill.[7] Similarly, the carbon conversion efficiency used in the present study was recently defined as follows:

\[
\eta_{\text{Carbon}} = \left(1 - \frac{m_{\text{Carbon, Fuel}}}{m_{\text{Carbon, TOC}}}\right) \times 100 \tag{2}[7]
\]

In eq. 2, \(m_{\text{Carbon, Fuel}}\) the mass flow rate of fuel carbon, \(\eta_{\text{Carbon}}\) is the carbon conversion efficiency, and \(m_{\text{Carbon, TOC}}\) the mass flow rate of the organic carbon in GL (GL TOC).

3 Results and discussion

3.1 Syngas composition

While the CO\(_2\) content in syngas decreased with increasing PO fraction, the CO and H\(_2\) contents increased almost linearly, as shown on Figure 3a. Since the increase was less pronounced for H\(_2\), the H\(_2\)/CO ratio decreased from 1.36 for BL to 1.23 for the 20% PO blend. Seeing as the fuel inorganic content decreased with increasing PO fraction, the increases in H\(_2\) and CO yields can be attributed to the resultant reduction in reactor thermal ballast, which meant that fewer oxidation reactions were required to reach the gasification temperature. Accordingly, the amount of carbon bound to sodium and potassium in smelt also decreased with increasing PO fraction. The effect was so pronounced that, in spite of 5%-points lower fuel carbon throughput compared with BL, the 20% PO blend actually resulted in a higher combined yield of CO and CO\(_2\) on a mass basis. Overall, the use of a 20% PO blend led to a 17% reduction in the additional oxygen demand per mole of H\(_2\)+CO produced.

Figure 4a shows that the standard temperature setting, which is denoted by a syngas CH\(_4\) fraction of 1.2 mol% yielded the highest CO and H\(_2\) flow rates for both BL and the 15% PO blend. The increase in reactor temperature from the “cold” to the “standard” setting led to a 7% increase in H\(_2\) flow rate. However, a further increase in temperature promoted the production of CO\(_2\) at the expense of CO, while the H\(_2\) flow rate also exhibited a marginal fall.

The ROC value of a given fuel can be calculated easily provided composition data is available. Hence, in addition to use as a means of differentiation between fuels, under certain circumstances it can also be used as a tool for predicting yields of major syngas species as a function of fuel oxygen content. On Figure 4a, the flow...
rates of H₂, CO and CO₂ for the six points representing four different fuel compositions show a partial correlation with ROC to varying degrees. The yields of all three components are determined by the water-gas shift reaction controlled by thermodynamic equilibrium. Moreover, as was alluded to in section 2.2, due to the effect of changes in e.g. the alkali/C ratio, parameters such as heating value and by extension gasification temperature and additional oxygen vary non-linearly with the O/C and the H/C ratio. This is partly responsible for the inability to qualitatively identify variations in fuel composition from changes in ROC alone. At the same time, the absence of a correlation with the rate-controlled CH₄, and to a lesser extent the only partially equilibrium-controlled H₂S can be seen clearly on Figure 4b. In the case of CH₄, the changes in yield are solely a function of temperature, which is regulated by the amount of added oxygen, and thus described adequately by λ.

3.2 Reactor temperature

The CH₄ content of both BL and the 15% PO OPs is plotted as a function of the temperatures recorded by the upper, middle and lower arrays of thermocouples (TCs) at the “cold”, “standard” and “hot” temperature settings in Figure 5. In comparison with BL, the 15% PO blend yielded slightly higher temperatures at all three positions for the same CH₄ content. The results in Figure 5 also confirm that the good correlation between the measured temperatures and syngas CH₄ for BL[8] holds true for the PO/BL blends as well. For the 15% PO blend, the correlation coefficients between the upper, middle, and lower temperatures and CH₄ were -0.99, -1.00 and -0.74. The correlations are particularly good for the upper and middle arrays which are located closer to the flame than the lone bottom TC, which, when functional, is more likely to provide readings representative of syngas temperature at reactor exit. Note that the present results are in agreement with observations that were made during the gasification of sulfite thick liquor in an earlier study.[8]

The temperature readings from the TCs mounted in the reactor wall are susceptible to conductive interference from the wall and radiation from the very hot flame in the upper part of the reactor. However, experience has shown that the recorded readings can consistently reflect and mirror changes in operating conditions over a single experimental run. The temperature rises recorded in the present study are believed to be inconsequential in terms of their impact on the life of the refractory lining.

Syngas from the blends was very clean as, irrespective of fuel composition, C₆H₆ was the only higher hydrocarbon present in amounts greater than 20 ppm. Figure 6 shows that the flow rate of C₆H₆ increases with increasing CH₄ for both BL and the 15% PO blend. Interestingly, the blend yielded noticeably less C₆H₆ than BL.
at nearly the same CH4 flow rate and the difference grew larger with decreasing temperature. The phenomenon is currently under investigation.

3.3 Sulfur release

The fraction of feedstock sulfur released as H2S, which is also referred to as the sulfur split, varied between 31-35% for the PO/BL blends and 28-31% for BL. Figure 3b shows that the decrease in fuel sulfur content with increasing PO fraction resulted in a corresponding decrease in the amount of sulfur release as H2S. As shown on Figure 4b, the H2S flow rate decreased by 6-7% between the “hot” and the “cold” temperature settings for both BL and the 15% PO blend. The extent of the sulfur released in gaseous form has been shown to reach a maximum at ~ 500-600°C,[21] and higher temperatures are thought to favor sulfur recapture.[22] The sulfur that is either recaptured by volatilized sodium or retained in smelt reacts with steam and CO2 according to the reaction in eq. 3.

\[
\text{Na}_2S (l) + H_2O(g) + CO_2(g) = Na_2CO_3(l) + H_2S (g) \to \Delta H_r = -169.8 \text{kJ/mol} \text{ (3)}
\]

A thermodynamic equilibrium study of BLG found around two-thirds of the feedstock sulfur in the gas phase as H2S at temperatures above 800°C and pressures above 20 bar.[6] However, the sulfur split for both the blends and BL shows that this was clearly not the case in the present study. Consequently, the reaction in eq. 3 is only in partial thermodynamic equilibrium, and the final division of fuel sulfur between smelt and syngas at the exit of the reactor is also subject to kinetic limitations.

According to Le Chatelier’s Principle, an increase in reactor temperature would be expected to lead to an increase in Na2S formation at the expense of H2S, as the reaction in eq. 3 shifts to the left. A partial shift did occur, as the fraction of gas-phase sulfur decreased with temperature by up to 4%-points for both BL and the 15% PO blend. On the other hand, the split was found to increase with PO fraction, by up to 6%-points for the 20% PO blend. In this case, the partial equilibrium is affected not only by the temperature, which increases only slightly with PO fraction, but also by the significant variations in the concentrations of the gaseous components.

Similar to previous studies,[4,7] a trivial amount of sulfur was also released in the form of COS at all OPs. The release was in the range 83-96 ppm and it was not possible to identify any correlation with fuel composition due to the hydrolysis of COS in the quench tube.[4] The molar fraction of N2 in syngas did not exceed 1.6% for any of the OPs. As the temperature of the gasification products falls after entering the quench tube, the water-gas
shift reaction produces more CO₂ and H₂. The extent of this shift, which is influenced by the orientation and flow rate of the cooling sprays,[4] could not be quantified, but the spray flow rates were set at 600 kg/hr to ensure constant cooling rates.

3.4 GL composition

Table 4 shows that aside from HCO₃⁻, which is dependent upon the magnitude of CO₂ absorption, the flow rate of the other element and ions decreased in proportion, albeit not wholly, with fuel inorganic fraction. Consequently, with the exception of the slightly anomalistic 15% PO OP, the GL became more dilute with increasing PO fraction. In principle, the elemental concentrations in GL are a product of fuel inorganic content and the amount of water added to the GL dissolver through the three water streams shown on Figure A.1 in the Supplementary Information. Although these streams provide a means of regulating GL concentration, due to the design and present set-up of the cooling system, the range of possible concentrations is constrained by limits on minimum flows. Hence, in the interest of maximizing operational stability, the water flows into the GL dissolver were not reduced in proportion to the expected reduction in smelt flow. In theory, the system can be optimized to better regulate inflows and increase the TTA by rebuilding the lower part of the gasifier. It has previously been shown that some of the syngas CO₂ is absorbed in the GL,[4] which results in the destruction of OH⁻, and the formation of HCO₃⁻ ions. The concentrations of these ions, which were present in all GL samples, did not appear to vary systematically with fuel composition.

In Kraft pulping, any sulfur present in a form other than Na₂S or K₂S does not play an active role in the cooking process, which means that sulfide reduction efficiency needs to be maximized. Sulfur reduction efficiency values of 100% within measurement uncertainty limits had previously been reported in an earlier study on the gasification of spent sulfite liquor.[8] Interestingly and somewhat unexpectedly, as seen in Table 4, the HS⁻ concentrations found in the GL were consistently lower than total S concentrations for both BL and the blends. At the same time, the correlation co-efficient between the HS⁻ and the total S concentrations was 0.90, which supported the relative accuracy of the measurements. The methods used for the determination of HS⁻ and total S concentrations in GL have specified relative measurement uncertainties of 15% and 10%, which is of the same order of magnitude as the differences between the values (10-30% relative to HS⁻). Moreover, GL from the BLG pilot plant is extremely sensitive to oxidation during sample preparation, which makes the quantification of reduced sulfur forms, such as sulfide ions, very difficult. Consequently, a complete characterization of the GL
sulfur species could not be carried out. Given the high reduction efficiencies seen previously, the differences
between total S and HS⁻ concentrations may be due to systematic analysis-related errors. Nonetheless, in light of
the above results and given the significance of sulfur recovery, the possibility of the presence of non-reduced
forms of sulfur in GL needs to be considered in future work.

The changes in the total organic carbon, total inorganic carbon and sludge content with increasing PO fraction
are shown in Figure 7. GL sludge fractions and TOC concentrations in the GL filtrate from both the blends and
BL were comparable and did not vary systematically. In contrast, as expected, the TIC content decreased linearly
since it is directly related to fuel inorganic content. Carbon found in formate ions constituted 23–41% of the TOC
in the GL filtrate from the PO/BL blends, and 24–49% from BL. The rest of the GL TOC is believed to be
mainly tars condensed during quenching and gas cooling as discussed in a recent publication.[7] However, in the
absence of a method for detailed TOC characterization, it is not possible to go much beyond reasoned
speculation. In the aforementioned study, the carbon present as formate had made up 10–28% of GL TOC and
measured formate concentrations had correlated reasonably well to the partial pressure of the CO in syngas.[7]
However, such a correlation was not found here for reasons that are not presently clear.

Figure 8 shows that, irrespective of fuel composition, neither GL TIC nor GL sludge showed a meaningful
change with temperature. While GL TOC did vary for both BL and the 15% PO blend, the changes did not
appear to be systematic. In both Figures 7 and 8, the error bars on the TOC concentrations represent an estimated
measurement uncertainty of 15%. It can be seen that although the uncertainties overlap partially, the range of the
variations exceeds measurement uncertainty, which was also found to be the case in an earlier study.[7] Coupled
to the fact that TOC variation not appear to be a function of the most probable process parameters such as fuel
composition, temperature or load, this points to the presence of currently unknown, non-controllable factors
which influence GL TOC.

3.5 Carbon conversion efficiency

The gasification of the PO/BL blends yielded carbon conversion efficiencies of 98.8–99.5%. These values
increase to 99.0–99.7% if the carbon present as formate in GL is considered “converted” for the purpose, given
its hypothesized origin in syngas CO. The completeness of conversion was also supported by the absence of any
detectable unconverted char in GL. Char gasification is the rate-limiting step controlling carbon conversion and it
is greatly facilitated by the intrinsically high reactivity of alkali-rich BL char.[9] A plot of the carbon conversion
efficiencies for all the OPs as a function of their ROC values (not shown) found there to be no correlation between the two variables. It may thus be concluded that the changes in $\eta_{\text{Carbon}}$ were independent of changes in blend ratio, fuel composition and temperature. As a corollary, the decrease in alkali loading with increasing PO fraction did not have a discernable effect on carbon conversion in the range studied.

### 3.6 Material and energy balance

The overall mass balance closures ranged from 94% to 100% and averaged 97% for both BL and the blends; the deviations in the closures seemed to have been independent of the fuel used. The discrepancy in the carbon mass balance closures did not exceed 4% for any of the OPs. However, in comparison, with a mean closure of 104%, a maximum discrepancy of 19% and a standard deviation of 7.4%, the sulfur balances closed less well. In agreement with past observations, the energy balance closures did not deviate by more than 5%.[7] See Appendices A1 and B1 in the Supplementary Information for an extended discussion and a detailed breakdown of the overall mass and energy balances by operation point.

### 3.7 Cold gas efficiency

In energetic terms, the value of increasing the PO fraction at a constant thermal load can be clearly seen from Figure 9a. As discussed in section 3.1, the CO and $\text{H}_2$ contents in syngas increased markedly with increasing PO fraction at the expense of $\text{CO}_2$. As a result, both $\text{CGE}_{\text{Power}}$ and $\text{CGE}_{\text{Fuel}}$ also increased. In comparison with BL, the 20% PO blend yielded a 7%-point higher $\text{CGE}_{\text{Fuel}}$, a 7%-point higher $\text{CGE}_{\text{Power}}$ and a 5%-point higher $\text{CGE}_{\text{Fuel} + \text{S-free}}$. $\text{CGE}_{\text{Fuel} + \text{S-free}}$ is the ratio of syngas LHVFuel, which is presented in Table B.2 of the Supplementary Information, and fuel LHVS-free, which is influenced by fuel S fraction. The decrease in syngas $\text{H}_2\text{S}$ content with increasing PO fraction meant that while it accounted for, on average, approximately 5% of LHV Power in the syngas from the BL, the same figure dropped to only 3.4% in the syngas from the 20% PO blend.

Figure 9b shows that due to the presence of CO and $\text{H}_2$ yield maxima, the potential for fuel production peaked at the “standard” temperature setting. Syngas contained significantly less CO and $\text{H}_2$ at the lower temperature setting, while at the higher temperature setting some of the CO was oxidized to $\text{CO}_2$, thereby resulting in a slightly lower $\text{CGE}_{\text{Fuel}}$. Meanwhile, changes in $\text{CGE}_{\text{Power}}$ are closely linked to the $\text{CH}_4$ content of syngas for a given fuel composition. At the “cold” temperature setting, $\text{CH}_4$ made up approximately 9% of syngas LHV. Due to the conversion of some of this $\text{CH}_4$ into CO and $\text{CO}_2$, the share dropped to 5-6% at the “standard” temperature.
setting. Consequently, $\text{CGE}_{\text{power}}$ at the “standard” temperature might be expected to be slightly lower, but as can
be seen from Figure 9b, the values of $\text{CGE}_{\text{power}}$ at the “high” and “standard” setting are very similar, which is
very likely due to experimental error. At the “hot” temperature setting, much of this CH$_4$ was converted to CO$_2$,
thereby leading to a decrease in syngas heating value. It is likely that the “standard” temperature setting
represents a close to optimal point for biofuel production within the operating envelope of the gasifier.

4 Concluding remarks

The results from this study demonstrate that a pilot-plant designed for the gasification of BL needs only minor
modifications, such as the addition of a PO/BL mixer, in order to successfully gasify PO/BL blends. In general,
the blending of BL with PO had a notably positive impact on the performance of the gasification process.
Importantly, carbon conversion did not vary systematically with fuel composition, which shows quite clearly that
the addition of up to 20% PO on a mass basis does not degrade the catalytic activity of BL Na. There were no
signs of an increase in either soot or tar formation. The blends yielded cold gas efficiencies that were markedly
greater in comparison to those of BL at the same thermal load.

The composition of syngas from unblended BL and the 15% PO blend exhibited largely similar behavior in
response to changes in temperature; in both cases, the “standard” temperature setting appeared to represent the
optimum for biofuel production. In comparison with unblended BL, the oxygen consumption of PO/BL blends
was higher per kg of feed, but lower per MW of syngas H$_2$+CO. It is believed that ROC can be useful as a tool
for predicting trends in yields of major syngas species from ash-free biomass feedstocks for varying feedstock
composition and gasification temperature.

The fate of sulfur is of significant consequence to the recovery of pulping chemicals and the integration of BLG
with a pulp mill. The fraction of sulfur that ends up in the syngas was somewhat higher for the PO/BL blends
than for BL. Due to analytical difficulties the sulfur reduction efficiency was uncertain. Based on the results
from this study, the gasification of blends with even higher PO fractions appears to be practically feasible. The
mixing characteristics of the PO/BL blends are currently the subject of active research. Future work in this area
is needed on (i) method development for better characterization of GL TOC, (ii) quantification of the effect of
long-term variations in fuel composition on process performance, and (iii) study of the sulfur chemistry in GL
and the syngas cooling system.
Supplementary Material: Appendices A and B

Gasifier material balance (A1) and Gasifier energy balance (B1).

Acknowledgement

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Figure captions

Figure 1. The major process components and key media streams.

Figure 2. \( \lambda \) as a function of ROC for BL (triangles) and the PO/BL blends (squares).

Figure 3. The change in the amounts of (a) CO (circle), CO\(_2\) (star) and H\(_2\) (square) as well as (b) H\(_2\)S (diamond) and CH\(_4\) (triangle) with blend ratio (0-20\%) at approximately constant syngas methane content.

Figure 4. The changes in (a) syngas CO (circle), CO\(_2\) (star), H\(_2\) (square) as well as (b) syngas H\(_2\)S (diamond) and CH\(_4\) (triangle) contents with temperature for BL (solid) and a 15\% PO blend (hollow).

Figure 5. The correlation between CH\(_4\) and reactor temperature for both BL (solid) and the 15\% PO blend (hollow). The upper (diamond), middle (square) and lower (triangle) arrays represent temperature measurements along the height of the reactor.

Figure 6. The flow rate of C\(_6\)H\(_6\) as a function of CH\(_4\) (and thus temperature) for both BL (solid) and the 15\% PO blend (hollow).

Figure 7. The effect of blend ratio (0-20\%) on sludge (square), TOC (triangle) and TIC (circle) concentrations in GL.

Figure 8. The variation in suspended solids (sludge) (square), TOC (triangle) and TIC (circle) contents in green liquor with temperature for BL (solid) and the 15\% PO blend (hollow).

Figure 9. CGE\(_{\text{Power}}\) (triangles), CGE\(_{\text{Fuel}}\) (circles) and CGE\(_{\text{Fuel+S-free}}\) (squares) on LHV basis for (a) the different fuel blends at standard temperature and (b) the 15\% PO blend at varying temperatures.
Table 1. The values of some key process variables for all the operating points (OPs)

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<th>10% PO</th>
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<th>BL-3 Std.</th>
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<th>BL Cold</th>
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Table 2. Elemental analyses of black liquor (BL) and pyrolysis oil (PO) (on a wet basis)

<table>
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<th>Unit</th>
<th>Average fraction</th>
<th>Lab</th>
<th>Measurement technique</th>
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<td>SPg</td>
<td>Element analyzer</td>
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<tr>
<td>H kg/kg BL</td>
<td>5.7%a</td>
<td>SPg</td>
<td>Element analyzer</td>
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<tr>
<td>N kg/kg BL</td>
<td>0.1%a</td>
<td>SPg</td>
<td>Element analyzer</td>
</tr>
<tr>
<td>Cl kg/kg BL</td>
<td>0.1%a</td>
<td>SPg</td>
<td>Ion chromatograph</td>
</tr>
<tr>
<td>Na kg/kg BL</td>
<td>13.9%b</td>
<td>ALSb</td>
<td>ICP- AESc</td>
</tr>
<tr>
<td>K kg/kg BL</td>
<td>2.6%b</td>
<td>ALSb</td>
<td>ICP- AESc</td>
</tr>
<tr>
<td>S kg/kg BL</td>
<td>4.5%b</td>
<td>ALSb</td>
<td>ICP- AESc</td>
</tr>
<tr>
<td>O kg/kg BL</td>
<td>51.4%</td>
<td>-</td>
<td>By difference</td>
</tr>
<tr>
<td>Dry solids kg DS/kg BL</td>
<td>73.2%</td>
<td>Drying and weighing</td>
<td></td>
</tr>
<tr>
<td>HHV BL MJ/kg DS</td>
<td>11.75</td>
<td>SPg</td>
<td>Bomb calorimetry</td>
</tr>
<tr>
<td>LHV BL MJ/kg BL</td>
<td>7.91</td>
<td>-</td>
<td>from HHV BL</td>
</tr>
<tr>
<td>Pyrolysis Oil</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C kg/kg PO</td>
<td>37.6%</td>
<td>VTTi</td>
<td>CHN analyzerd</td>
</tr>
<tr>
<td>H kg/kg PO</td>
<td>7.8%</td>
<td>VTTi</td>
<td>CHN analyzerd</td>
</tr>
<tr>
<td>N kg/kg PO</td>
<td>0.1%</td>
<td>VTTi</td>
<td>CHN analyzerd</td>
</tr>
<tr>
<td>O kg/kg PO</td>
<td>54.5%</td>
<td>By difference</td>
<td></td>
</tr>
<tr>
<td>Dry solids kg DS/kg PO</td>
<td>70.1</td>
<td>VTTi</td>
<td>Karl Fischer titratione</td>
</tr>
<tr>
<td>TAN mg KOH/g</td>
<td>64.4</td>
<td>VTTi</td>
<td>Potentiometric titrationf</td>
</tr>
<tr>
<td>HHV BL MJ/kg DS</td>
<td>16.84</td>
<td>LTUJ</td>
<td>Bomb calorimetry</td>
</tr>
<tr>
<td>LHV BL MJ/kg BL</td>
<td>15.12</td>
<td>-</td>
<td>from HHV using composition data</td>
</tr>
</tbody>
</table>

aCalculated from two samples taken at the beginning and the end of the experimental run; bCalculated from 10 samples spread over the experimental run; cSS EN ISO 11885 (modified); dASTM D 5291; eASTM E 203; fASTM D 664; gSP Research Institute of Sweden (Borås); hALS Scandinavia, Luleå; iVTT Technical Research Centre of Finland Ltd; jLTU ENE Lab.
<table>
<thead>
<tr>
<th>Media</th>
<th>Component</th>
<th>Lab</th>
<th>Measurement Method</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>green liquor</td>
<td>Na, K, S</td>
<td>ALS&lt;sup&gt;d&lt;/sup&gt;</td>
<td>ICP-AES</td>
<td>SS EN ISO 11885 (modified)</td>
</tr>
<tr>
<td></td>
<td>Filtrate TIC&lt;sup&gt;e&lt;/sup&gt;</td>
<td>MoRe&lt;sup&gt;e&lt;/sup&gt;</td>
<td>Filtration</td>
<td>T 692 om -93</td>
</tr>
<tr>
<td></td>
<td>Filtrate TOC&lt;sup&gt;e&lt;/sup&gt;</td>
<td></td>
<td>TOC analyzer&lt;sup&gt;b&lt;/sup&gt;</td>
<td>ISO 8245</td>
</tr>
<tr>
<td></td>
<td>Suspended solids “sludge” content</td>
<td></td>
<td>acid titration</td>
<td>SCAN-N 32</td>
</tr>
<tr>
<td></td>
<td>CO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;, HCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>Invenvia&lt;sup&gt;f&lt;/sup&gt;</td>
<td>IC-CD&lt;sup&gt;j&lt;/sup&gt;</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>HS&lt;sup&gt;−&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>HCOO&lt;sup&gt;−&lt;/sup&gt;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>condensate</td>
<td>Na, K, S</td>
<td>ALS&lt;sup&gt;d&lt;/sup&gt;</td>
<td>ICP-AES</td>
<td>SS EN ISO 11885 (modified)</td>
</tr>
<tr>
<td></td>
<td>TIC</td>
<td>MoRe&lt;sup&gt;e&lt;/sup&gt;</td>
<td>TOC analyzer&lt;sup&gt;b&lt;/sup&gt;</td>
<td>ISO 8245</td>
</tr>
<tr>
<td></td>
<td>TOC</td>
<td></td>
<td></td>
<td>ISO 8245</td>
</tr>
<tr>
<td>syngas</td>
<td>All components</td>
<td>SP ETC&lt;sup&gt;g&lt;/sup&gt;</td>
<td>Gas chromatography&lt;sup&gt;i&lt;/sup&gt;</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<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>Invenvia AB, Stockholm; <sup>g</sup>SP Energy Technology Center, Piteå; <sup>h</sup>Shimadzu, Model TOC-5050; <sup>i</sup>Ion chromatography with conductivity detection; <sup>j</sup>Varian CP-3800.
Table 4. The concentrations of the most important ions and elements in green liquor from the three pyrolysis oil blends.

<table>
<thead>
<tr>
<th></th>
<th>BL only&lt;sup&gt;b&lt;/sup&gt;</th>
<th>10% PO</th>
<th>15% PO</th>
<th>20% PO</th>
</tr>
</thead>
<tbody>
<tr>
<td>S (mol/L)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.51</td>
<td>0.36</td>
<td>0.39</td>
<td>0.29</td>
</tr>
<tr>
<td>Na (mol/L)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.20</td>
<td>2.14</td>
<td>2.36</td>
<td>1.84</td>
</tr>
<tr>
<td>K (mol/L)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.34</td>
<td>0.24</td>
<td>0.26</td>
<td>0.20</td>
</tr>
<tr>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;- (mol/L)</td>
<td>0.21</td>
<td>0.18</td>
<td>0.18</td>
<td>0.21</td>
</tr>
<tr>
<td>HS&lt;sup&gt;-&lt;/sup&gt; (mol/L)</td>
<td>0.42</td>
<td>0.30</td>
<td>0.30</td>
<td>0.27</td>
</tr>
<tr>
<td>CO&lt;sub&gt;3&lt;/sub&gt;²⁻ (mol/L)</td>
<td>1.27</td>
<td>0.95</td>
<td>0.92</td>
<td>0.82</td>
</tr>
<tr>
<td>HCOO&lt;sup&gt;-&lt;/sup&gt; (mol/L)</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>Total Titrable Alkali (mol/L)</td>
<td>3.54</td>
<td>2.38</td>
<td>2.62</td>
<td>2.04</td>
</tr>
<tr>
<td>(S+2*CO&lt;sub&gt;3&lt;/sub&gt;²⁻+HCO&lt;sub&gt;3&lt;/sub&gt;⁻)/(Na+K) (mol/mol)</td>
<td>95%</td>
<td>103%</td>
<td>92%</td>
<td>104%</td>
</tr>
<tr>
<td>Sulfidity – S/(Na+K)² (mol/mol)</td>
<td>28.9%</td>
<td>29.9%</td>
<td>29.8%</td>
<td>28.5%</td>
</tr>
</tbody>
</table>

<sup>a</sup>S, Na and K concentrations have a measurement uncertainty of 10%; <sup>b</sup>The concentrations are averages of measurements from BL OPs at the same thermal load as the PO/BL blends.


Figure 3

(a) Flow rate [kmol/hr] vs. Fuel (Na+K)/C [mol/mol]

(b) Flow rate [kmol/hr] vs. Fuel (Na+K)/C [mol/mol]
Figure 4

(a) ROC [-] vs. Flow rate [kmol/hr] for different conditions: Cold, Standard, Hot.

(b) ROC [-] vs. Flow rate [kmol/hr] for different conditions: Cold, Standard, Hot.
Figure 5

The graph shows the relationship between reactor temperature (°C) and CH4 [kmol/hr]. The data points are represented by different markers and lines, indicating various conditions or experiments. The x-axis represents reactor temperature ranging from 940 to 1090 °C, while the y-axis represents CH4 production in kmol/hr from 0 to 6.
Figure 6

![Graph showing the variation of C6H6 with CH4 concentration for different temperatures (hot, standard, cold). The graph plots C6H6 concentration in mol/hr against CH4 concentration in mol/hr. The data points for each temperature are marked with distinct symbols: hot (triangle), standard (square), and cold (circle).](image-url)
Figure 7

[Graph showing relationships between Fuel (Na+K)/C [mol/mol] and various measurements such as TOC and sludge in g/L GL.]
Figure 9

(a) Cold gas efficiencies [%] vs. Fuel (Na+K)/C [mol/mol]

(b) Cold gas efficiencies [%] vs. ROC [-]

- Standard
- Hot
- Cold
Paper III

Thermodynamic Equilibrium Modelling of Catalytic Entrained-Flow Gasification of Biomass
Thermodynamic Equilibrium Modelling of
Catalytic Entrained-Flow Gasification of Biomass

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Abstract
Pressurised entrained-flow gasification has been identified as a suitable technology for the sustainable production of biofuels and biochemicals from a range of lignocellulosic biomass. Recently published research indicates that the addition of alkali catalysts to biomass feedstocks can allow high carbon conversion to be obtained at lower temperatures than would be possible without their use.

The main objective of this work was to investigate catalytic entrained-flow gasification of biomass for a wide range of elemental compositions using thermodynamic equilibrium calculations. The model used in the study was validated using data from a pilot-scale study of black liquor and pyrolysis oil co-gasification. Both liquid and solid cases were simulated by varying the elemental O/C, H/C and Na/C ratios in carefully chosen ranges to obtain compositions that were characteristic of real cases. It was found that elemental composition based empirical correlations which took into account fuel ash content provided significantly better predictions of the HHVs of alkali-impregnated biomass samples.

The results of the validation study showed that the model used in the study was able to predict the main components in syngas and smelt from the gasification of pyrolysis oil/black liquor blends to an acceptable degree of accuracy. Methane formation and the distribution of fuel sulfur between liquid and gas phase were found to be the two major deviations from equilibrium, which was in agreement with results previously obtained for pure black liquor.

The quantification of gasification performance using generic thermodynamic equilibrium calculations provides an efficient means of comparing the differences between fuels for a number of interesting process parameters. The results show that pressurised catalytic entrained-flow gasification of biomass-based fuels with O/C ratios in the range 0.5-1 and H/C ratios in the range 1-2 is thermodynamically feasible at a temperature of 1050°C with complete carbon conversion. The highest cold gas efficiencies were returned by solid compositions with low O/C and H/C ratios, while the largest H₂/CO ratios were returned by fuel compositions with the higher fuel moisture content of 25%.
1. Introduction

The importance of the catalytic activity of ash components in coal gasification is well known[1] and also addition of alkali catalyst to coal has been used[2,3]. Recently, alkali catalysis in biomass gasification has received a lot of attention, including studies of solid biomass[4–6], pyrolysis oil (PO)[7,8], and black liquor (BL) gasification[9], as well as co-gasification of BL with PO (see Paper II) and glycerol[10]. Black liquor contains high concentrations of alkali salts and thus possesses intrinsic catalytic activity[11–13], which is an important reason for the successful implementation of this technology for biofuel production in pilot scale[14]. Black liquor has even been used as an additive to provide catalytic activity during gasification of various fossil feedstocks[15–17].

The primary effect of alkali is to promote char gasification[18] which is often the rate limiting sub-process. For entrained flow (EF) BL gasification, alkali catalysis enables very high carbon conversion in a few seconds at relatively low temperatures of 1000-1100 °C[9]. For sawdust and other low-alkali solid biomass fuels, much higher temperatures are required to reach similar conversion in EF gasification[19,20]. If the temperature could be lowered to levels similar to those used for BL, it would lead to a number of advantages, including greater efficiency and a decrease in material wear. Experimental results with alkali impregnated biomass indicates that this may be feasible with further development[21]. In addition, the presence of alkali in liquid biomass blends has been shown to repress tar and soot formation during gasification at temperatures up to 1100°C[22]. The usefulness of various forms of thermodynamic equilibrium modeling as a relatively simple and cost-efficient method for studying and understanding gasification behavior has already been established for coal and a diverse range of biomass fuels[23]. Recently, it was shown that many aspects of EF BL gasification are well described by thermodynamic equilibrium[24]. The major deviations from equilibrium are present in methane formation and the distribution of sulfur between the two exit streams[24]. However, they do not significantly impair the ability to predict important parameters like cold gas efficiency (CGE) and added oxygen consumption.

Based on the above, alkali catalysis in gasification is of great interest to EF gasification of both liquid and solid biomass but it has not been studied systematically from a general viewpoint. The first objective of this work is to further validate the usefulness of the thermodynamic equilibrium model for EF catalytic gasification in industrially relevant scale using pilot scale data for co-gasification of BL and PO. A second objective is to use the validated model to study the theoretical performance of EF catalytic biomass gasification for a wide range of biomass compositions.

2. Equilibrium Modelling

The thermodynamic equilibrium calculations (TEC) were performed using the MATLAB-based SIMGAS model, which utilizes a non-stoichiometric approach in conjunction with the assumption of
ideal mixtures for both the gas and the inorganic smelt phase. The SIMGAS model was recently used to study entrained-flow gasification of alkali-rich spent pulping liquors by the present authors[24]. The reader is referred to this study for further details of the thermodynamic model and a comparison of the results with the commercial FactSage (GTT-Technologies, Aachen, Germany) suite.

2.1. Equilibrium Modelling

The suitability and accuracy of the model for the simulation of catalytic entrained-flow gasification of biomass was evaluated by validating the model using recent experimental data from the catalytic co-gasification of BL and PO. The inputs to the model consisted of the temperature, flow and composition of the streams entering the reactor, namely, fuel, oxygen and a small amount of nitrogen. For validation, the model was executed in a mode where the equilibrium temperature was calculated by specifying the experimentally determined heat loss and iteratively solving the energy balance over the reactor.

It has been shown that thermodynamic equilibrium calculations can be highly sensitive to errors in fuel composition data[24]. In this instance, similar to the approach adapted in the experimental study, the composition of BL solids was assumed to be constant at all OPs, while the variations in solids fraction, which were captured by an online refractometer, were represented in the simulation. The solids composition was assembled from experimentally determined averages of Na, K, and Na concentrations in samples from all ten OPs, averages of experimentally determined C, H, N, Cl concentrations (on a dry basis) in samples taken from two OPs at either end of the experimental run. Oxygen was calculated by difference.

The use of a composition that is assembled from averaged elemental concentrations with varying measurement uncertainties does disregard any compositional variations that may have occurred over the experimental run. In practice, the high relative measurement uncertainties of up to 10% that are associated with the determination of several of these values render the use of a more nuanced approach impractical for studies that do not specifically aim to evaluate model sensitivty to input data.

2.1.1. Experimental Dataset

The model was validated using a study of BL and PO co-gasification that had been carried out in a pressurized, oxygen-blown entrained-flow gasifier at the LTU Green Fuels pilot plant in Piteå, Sweden. Several detailed descriptions of the plant as well as the gasification process have been provided in previous studies[9,25–28] by a number of different authors and the readers are referred to the enclosed references for further details.

The experimental dataset used for validation was made up of ten individual operating points (OPs) representing eight different settings. These were obtained by varying BL/PO blend ratio in the range 0-
20% on a mass basis and altering the amount of added oxygen to yield three temperature settings denoted by syngas CH₄ fractions of 0.5 mol%, 1.1 mol% and 2.1 mol%. Although gasifier thermal load was kept constant at around 2.7 MWth for all the operating points, the difference in the heating value of black liquor and the more energy-rich pyrolysis oil meant that fuel mass flow decreased with increasing blend ratio. The details of experimental conditions and fuel feed data for each OP can be seen in Table 1 of the experimental study (see Paper II). In the experimental study, the composition of syngas was determined from samples that were collected from a point downstream of the cooler where the gas temperature was ~ 30°C.

The availability of detailed mass and energy balances as well as process data for each OP enabled the comparison of not just syngas but also smelt composition, which primarily comprised alkali carbonates and sulfides. The study included averaged reactor temperature measurements from two, and when possible three, thermocouples at three points along the length of the reactor. The readings from the two uppermost thermocouple arrays are affected by the proximity of the flame to a greater extent than those from the bottom thermocouple, which is considered more representative of the temperature of the exiting gas. Comparisons between predicted and measured temperatures need to be carried out in awareness of the fact that, besides the effect of flame radiation, the latter are also influenced by the temperature of both the gas and the ceramic lining.

2.2. Simulation Design and Setup

In the generic simulations that were carried out to characterize the performance of catalytic gasification, elemental ratios were used to visualise and compare the gasification performance of different feedstocks. Four parameters were varied in the thermodynamic equilibrium calculations of catalytic entrained-flow gasification: the alkali/carbon ratio, the O/C ratio, the H/C and fuel moisture content. All ratios were calculated from fuel fractions on a molar basis in dry biomass.

The alkali/C ratio was varied between 0.01 and 0.45. A wide range of ratios was picked to represent both the high [29] and the low [4] ends of the alkali-loading spectrum. Kraft BL is the most pertinent example of the former. As seen from Table 2, it has an elemental alkali/C ratio of between 0.4-0.45 on a dry basis. This is an order of magnitude greater than the elemental alkali/C ratios of the alkali-impregnated pine wood samples (see Table 2) whose suitability for catalytic gasification was evaluated in a recently published work [4].

The difference in the alkali loads can be attributed to the fact that the alkali content of black liquor is well in excess of that needed for tar and soot-free fuel conversion at low temperature [30]. From an energy perspective, the presence of excess alkali decreases the heating value of the fuel and increases the quantity of the oxidation reactions that are required to raise the products in the reactor to gasification temperature. The use of alkali salts for the impregnation of biomass also leads to a small
decrease in the heating value due to carbon leaching[21], although it was discovered that this decrease is not strictly correlated to the elemental alkali/C ratio in the fuel. Thus, it makes sense to limit the alkali loading to the smallest value that would maximise energy input while still allowing the realisation of the catalytic effect for efficient conversion.

The elemental O/C ratio was varied between 0.4 and 1.1. The chosen range covers the ratios seen in different biomass components such as hemicellulose and lignin as well as most biomass feedstocks that would be considered likely candidates for catalytic gasification. This was based on the results from a wide-ranging survey carried out in the early 1990s[31]. In the survey, the elemental H/C and O/C ratios of biomass fuels (on a molar basis) were found to lie between 1-2 and 0.3-1, respectively. TECs were carried out for the alkali/C and O/C ranges specified above at three different elemental H/C ratios of 1.2, 1.5 and 1.8 and two different fuel solids contents of 75 wt% and 95 wt%. The H/C ratios were chosen since they typified three biomass-based feedstocks with very different elemental compositions, namely, lignin, pine wood (including alkali-impregnated pine wood) and cellulose (see Table 2).

Pressurized entrained-flow gasifiers can process both liquid [14] and solid biofuels [32], although the liquid variants are more numerous and technologically advanced[33]. The 95% dry solids represents a pulver-fed gasification process, while 75% dry solids represents liquid feedstocks as exemplified by PO and BL, both of which have water contents of ~25 wt%. Vinasse is a third liquid biofuel that can be a relevant feedstock for catalytic gasification in the future due to its high alkali content[34]. By performing the thermodynamic equilibrium calculations at two different solids fraction, not only were both solid and liquid feeding options evaluated in the study, but the effect of dry solids fraction on syngas composition and cold gas efficiency for the whole range of chosen O/C,H/C and Na/C ratios was also quantified.

Except BL, most processed biomass feedstocks of interest to entrained-flow gasification, such as pine wood, oak bark and pyrolysis oil contain small to negligible amounts of nitrogen and sulfur. Consequently, all fuels were assumed to be composed of carbon, hydrogen, oxygen and sodium only. Since it was based on the pilot-scale unit used in the co-gasification study, the ‘virtual’ gasifier in the simulations represented an auto-thermal, pressurized process. All thermodynamic equilibrium calculations were performed at 31 bar. The choice of values for some parameters was influenced by the wish to simulate cases that would mirror commercial-scale operation in an integrated biorefinery set-up. As a result, the heat loss through the reactor walls was set to 0.7% of fuel higher heating value (HHV) even though measurements show that the heat loss in pilot-scale can be as high as 6% of fuel HHV at a thermal load of ~2.8 MW. The reactor temperature was set at 1050°C and the amount of oxygen required was returned by the model for each calculations. The choice of 1050°C as the reactor temperature for catalytic gasification was motivated by the fact that both pure BL and PO/BL blends
with up to 20% PO have been shown to yield conversion efficiencies of 99% at temperatures between 1000-1100°C (See Paper II). These fuels have elemental alkali/C ratios of 0.42 and 0.35, respectively.

The carbon conversion efficiencies of solid alkali-impregnated biomass feedstocks have not been calculated experimentally. However, samples with elemental alkali/C ratios as low as 0.05 took around 14 seconds to reach 99% carbon conversion in particle-scale simulations[21]. For comparison, typical residence times in entrained-flow gasifiers are around 10-12s. Additionally, the authors of the aforementioned study concluded that their kinetic models overestimated conversion times in most cases. Given the above, it is conceivable that biomass feedstocks with elemental alkali/C ratios around 0.05 can yield high carbon conversion efficiencies at temperatures between 1050°C and 1100°C in particle residence times that are characteristic of entrained-flow gasifiers. On the other hand, biomass fuels with significantly lower alkali/C than 0.05 are not likely to reach complete conversion in relevant times at the chosen temperature.

The performance of the model was quantified using cold gas efficiency on a lower heating value basis as a measure of energy efficiency, the external oxygen demand per unit CO+H₂ (EOD) as a measure of external oxygen demand and the H₂/CO ratio as an indicator of syngas composition. EOD offers a relatively simple means of comparing the efficiency of external oxygen use at difference process settings for a range of feedstock. The H₂/CO ratio in cooled raw syngas is an important parameter for the production of methanol and synthetic fuels since it directly determines the load requirements of the water gas shift reactor.

2.3. Selection of Empirical Correlation for Heating Value Estimation

In order to minimize discrepancies in energy balance closures, it was imperative that the heating value of the varying fuels be determined with a reasonable degree of accuracy over the full range of specified fuel Na/C ratios. Many empirical correlations that are used to calculate heating values of biomass-based fuels from their elemental compositions only take into account the carbon and hydrogen, and more rarely, sulfur, contents. They may yield poor predictions in the case of ash-rich fuels, of which alkali-impregnated biomass with high Na/C ratio may be considered a subset due to the absence of appropriate data points from the derivation dataset.

Before performing the modelling, a survey of elemental composition-based empirical correlations was undertaken in order to identity suitable options, which are presented in Table 1 for more detailed benchmarking. These correlations were selected on the basis of their applicability to ash-rich biomass fuels, evaluations in a recent review [35] and the frequency of their appearance in topical publications from the last decade [36,37]. The choices were also informed by the desire to compare the predictive capabilities of correlations that take into only carbon and hydrogen with those that also consider the ash content of fuels.
Table 1. Details of the four elemental composition based empirical correlations for the prediction of higher heating value that were validated with experimental data.

<table>
<thead>
<tr>
<th>Author(s) and Publication Year</th>
<th>Correlation (HHV, MJ kg⁻¹ dry basis)</th>
<th>Dataset type</th>
<th>R² coefficient</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheng and Azevedo, 2005 [38]</td>
<td>-1.3675 + 0.3137C + 0.7009H + 0.0318O*A</td>
<td>209 wide-ranging biomass samples</td>
<td>0.834</td>
<td>Chosen due to an extensive, purely biomass-based dataset and the implicit inclusion of ash content in the correlation.</td>
</tr>
<tr>
<td>IGT, 1978 [39]</td>
<td>0.341C + 1.322H – 0.12O – 0.12N + 0.0686 S – 0.0153 Ash</td>
<td>More than 700 coal samples</td>
<td>0.69³⁰</td>
<td>Chosen due to the comprehensive coal-based dataset and the explicit inclusion of ash content in the correlation.</td>
</tr>
<tr>
<td>Chaniwala and Parikh, 2002 [40]</td>
<td>0.3491C + 1.1783H + 0.1005S – 0.1034O – 0.0151N – 0.0211A</td>
<td>225 samples including gaseous fuels, liquid fuels, wastes, biomass materials and biomass chars</td>
<td>0.73³¹</td>
<td>Chosen due to the comprehensive and wide-ranging dataset as well as the explicit inclusion of ash content in the correlation.</td>
</tr>
<tr>
<td>García et al., 2015 [36]</td>
<td>1.59C² + 154.5C + 7464</td>
<td>100 (Spanish) biomass samples</td>
<td>N/A</td>
<td>Chosen as a recently proposed carbon-only correlation derived from a solid biomass-heavy dataset.</td>
</tr>
</tbody>
</table>

³⁰O*A is defined as the sum of the contents of oxygen and other elements (including S, N, Cl, etc.) in the organic matter, i.e. O = 100-C-H-Ash; ³¹Independently calculated by Sheng and Azevedo[38]

The evaluation of the chosen correlations was performed by comparing the estimated and measured HHVs of a total of seventeen samples: two varieties each of kraft black liquor and flash pyrolysis oil as well as hemicellulose, cellulose, kraft lignin, organosolv lignin, and seven other biomass-based feedstocks including four woodchip samples that were impregnated using sodium or potassium salts in different ionic concentrations. The elemental composition of the selected feedstocks on dry basis, their experimentally measured heating value and molar O/C, H/C and Na/C ratios are provided in Table 2. As evident from the table, taken together, they represent a selection that cover large areas of the specified H/C and O/C ranges as well as both low and high alkali loadings. The heating values and the elemental compositions of pine wood and the four alkali impregnated pine wood samples were taken from a recent kinetic study of wood char from the gasification of alkali impregnated biomass[10].
The elemental compositions and experimentally determined higher heating values of peat, bagasse, oak bark and saw dust were taken from Parikh and Channiwala[40], while those of hemicellulose, cellulose, kraft lignin, organosolv lignin as well as one variety each of kraft black liquor and flash pyrolysis oil were sourced from the Phylis 2 database maintained by ECN, Netherlands and co-funded by the EU 7th Framework Programme through the BRISK project[41]. The other variety of kraft black liquor and flash pyrolysis oil had been analysed at SP, Sweden and VTT Research Institute of Finland, respectively.

Table 2. Characteristic elemental ratios (on a dry basis) and HHVs of the fuels in the experimental dataset used for the selection of the most appropriate correlation for heating value prediction.

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>1M NaOH¹</td>
<td>17.3</td>
<td>1.53</td>
<td>0.73</td>
<td>0.06</td>
<td>[4]</td>
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<tr>
<td>0.5M Na₂CO₃²</td>
<td>18.4</td>
<td>1.56</td>
<td>0.70</td>
<td>0.02</td>
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<td>0.1M NaOH³</td>
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<td>0.69</td>
<td>0.01</td>
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<tr>
<td>0.05M K₂CO₃¼</td>
<td>19.4</td>
<td>1.56</td>
<td>0.68</td>
<td>0.01</td>
<td>[4]</td>
</tr>
<tr>
<td>Saw Dust</td>
<td>20.0</td>
<td>1.48</td>
<td>0.64</td>
<td>N/A</td>
<td>[40]</td>
</tr>
<tr>
<td>Oak Bark</td>
<td>19.4</td>
<td>1.29</td>
<td>0.59</td>
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<td>[40]</td>
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<td>0.66</td>
<td>N/A</td>
<td>[40]</td>
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<tr>
<td>Kraft black liquor</td>
<td>12.5</td>
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<td>Kraft black liquor</td>
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3. Results and Discussion

3.1. Model Validation with Experimental Data

3.1.1. Predicted Equilibrium Temperature

The effect of an increase in fuel PO fraction on both predicted and measured temperatures is plotted in Figure 1. It shows a strong positive correlation between fuel PO fractions and predicted, but not measured, temperatures. The disagreement between the predicted and experimentally measured temperature exceeded 120°C for the 20% PO blend. Readings from the thermocouple arrays located in the middle and near the top of the reactor (see “Section A1 under “Supplementary Material”) also confirmed the presence of this difference.

Figure 1. A comparison of predicted (diamond) equilibrium temperatures for both BL (hollow) and BL/PO blends (solid) with an averaged measurement from the bottom thermocouple in the reactor.

It has been shown that predicted equilibrium temperatures can be very sensitive to relatively small variations in fuel composition for BL[24]. However, both the predicted and the measured temperatures lay quite near each other for the BL only OPs. This meant that compositional variations in BL could not explain the predicted temperature change with blend ratio. The elemental composition and the moisture content of the PO used in the experimental study were determined from the analysis of a sample that was taken directly from the storage tank in the middle of the experimental run. The PO in the tank was stirred continuously and kept in circulation to ensure homogeneity, which is believed to have been attained throughout the experimental run and led to the minimisation of day-to-day
variations in oil composition. Hence, PO elemental composition analysis errors were identified as a possible source behind the trend. This could be further broken down into errors in the measurement of (a) moisture content and (b) solids composition.

A sensitivity analysis of the two potential causes was carried out in order to quantify the impact of potential variations on predicted equilibrium temperature. First, PO moisture content was varied in increments of 2%-units. This increment was chosen because a variation of 2%-units was within the standard deviation of the measurement method [43] and corresponded to an increase of 0.25%-units in the carbon fraction of PO on a wet basis. However, the resulting variations in predicted temperatures were an order of magnitude smaller than the differences between experimental and measured values and appeared to be largely independent of changes in blend ratio. Thus, any errors in the determination of moisture content are not likely to have contributed significantly to the over-prediction of equilibrium temperature.

Second, the oxygen fraction of PO solids was also varied in increments of 2%-points. This meant that the carbon and hydrogen content in PO solids changed with the increment in proportion to their respective fractions in PO solids on an oxygen-free basis. For example, the baseline case (see Figure 2) had a molar O/C ratio of 0.572, while the case with 4%-points less oxygen had a significantly lower O/C ratio of 0.483 due to an increase in the fractions of carbon and hydrogen by 6.7%. For reference, the method used for the determination of carbon and hydrogen fractions in PO, ASTM D 5291, was found to have a relative uncertainty of 0.8% for carbon and 1.2-2.6% for hydrogen (95% confidence interval).
Hence, the change in carbon and hydrogen fractions with each increment was greater than the measurement uncertainty of the method.

The results of the analysis, which are plotted on Figure 2 for the baseline, O+2, O-2 and O-4 cases were revealing. In the case of the 20% blend, the predicted temperatures rose or fell by ~ 70°C for each 2%-point increment. Crucially, the magnitude of the change in the predicted temperatures for each increment also increased with the fraction of PO in the blends. This trend was particularly pronounced for the +2 case, which returned temperatures that moved still further away from the measured values. On the other hand, a move in the opposite direction towards a more carbon- and hydrogen-rich composition seemed to retard the rate of increase with increasing blend ratio. It also yielded temperatures that were in better agreement with the experimental measurements. This hints at an underestimation of the carbon and hydrogen content in PO solids due to errors in the elemental analysis.

Some idea of the sensitivity of the model to experimentally insignificant variations in fuel composition can be gathered from the fact that the increment used in the sensitivity analysis presented above corresponded to a decrease of 0.35%-points in the carbon content of the 20% PO blend. Given that the discrepancy in carbon balance closures ranges between 2-5%-points based on published experimental data,[9] these variations would have little impact on the mass balance and likely would not be picked up in an experimental study.

Note that the experimentally-measured heating value of the PO used in the study was kept constant in all TECs. Expectedly, the predicted temperature was sensitive to incremental changes in PO HHV. However, a sensitivity analysis (not shown) revealed that a 70°C change in the predicted temperature required an error of 12% in the PO HHV, which is much larger than the measurement uncertainty. Hence, any errors in HHV are unlikely to be the main reason behind mispredictions of equilibrium temperature for the PO/BL blends.

3.2. Syngas Composition

Figure 3a shows the changes in both CO and CO₂ flow as a function of blend ratio. The model successfully predicts the general trend for both components. The equilibrium of the system dictates that, unlike in reality, CH₄ flows are negligible for both pure BL and the PO/BL blends. The carbon and the hydrogen held up in methane are instead allocated to other species by the model. The allocation of the carbon in methane to CO and CO₂ by the model can be estimated by manually constraining CH₄ and comparing the CO and CO₂ yields with those from the unconstrained case. However, the actual amount of CH₄ in syngas, which varied between 0.1-0.6 kmol/hr in the experimental study (see Paper II) did not exceed more than 3.5% of the total carbon throughput of over 18 kmol/hr in syngas. Thus, while the underestimation of methane content undoubtedly leads to
an over prediction of both CO and CO₂, in practise, the error incurred remains small as long as the methane content in syngas remains low. Unlike CO and CO₂, the flow of H₂ is affected to a greater extent by the under-prediction of CH₄[24,45]. This likely contributed to the under prediction by the model, (see Figure 3b), although the disagreement with the measured flows was neither large nor did it exhibit a systematic trend with increasing blend ratio.

Equilibrium models have previously been shown to overpredict the amount of H₂S in syngas compared to experimental results[24]. However, in this study, the predicted H₂S flows (Figure 4) showed excellent agreement with experimental data for the PO/BL blends, whereas for pure BL OPs were they were over-predicted by a factor of 2. Recall that the model predicted significantly higher equilibrium temperatures for the blends. Consequently, the agreement between the predicted and the measured H₂S flows improves significantly with temperature. The accuracy of H₂S predictions has been shown to improve with an increase in reactor temperature[24]. Thus, it is likely that the excellent agreement seen here is simply due to the erroneous over-prediction of equilibrium temperature, which occasioned a coincidental agreement with experimentally obtained H₂S flows for the PO/BL OPs.

Since the predicted flows represent hot syngas at reactor exit, they fail to take into account reactions and interactions that take place during syngas cooling[28]. The compositions of all three major components and H₂S change as syngas undergoes quenching and cooling[28]. Note that, according to the model, the smelt from the gasification of BL is principally composed of carbonate, sulfide and
hydroxide salts of alkali in decreasing order of magnitude on a molar basis[24]. The smelt from the PO/BL blends (not shown) had a similar distribution.

Some of the CO₂ reacts with the alkali hydroxides in smelt to form alkali carbonates as shown in Eq 1. The occurrence of this reaction substantiated by the absence of hydroxide ions from GL samples. (see Table 3 in [9])

\[
2\text{NaOH}(aq) + \text{CO}_2(g) \rightarrow \text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(aq) \quad (1)
\]

Similarly, some of the CO₂ is also absorbed by GL, which leads to the formation of bicarbonate, as shown in Eq. 2.

\[
\text{Na}_2\text{CO}_3(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(aq) \rightarrow 2\text{NaHCO}_3(aq) \quad (2)
\]

The amounts of CO₂ that was absorbed by GL varied between 0.19-0.23 kmol/hr for the PO/BL blends. These values are based on the bicarbonate concentrations from the pilot-scale co-gasification study (see Table 4 in Paper II). Similarly, between 0.42-0.57 kmol/h of CO₂ reacted with the metal hydroxides, based on the molar flows predicted by the model. Taken together, these figures added up to between 4-7% of the CO₂ in the syngas at reactor exit for the PO/BL OPs that were modelled in this study. The numbers for the BL OPs were similar. The inaccuracies in the equilibrium H₂S prediction mean that yet another parameter that has a differential influence on the predicted CO₂ flows from the blends and BL is the partial equilibrium of the heterogeneous, rate-constrained reaction shown in Eq. 3, which determines the sulfur split between syngas and green liquor.

\[
\text{Na}_2\text{S}(l) + \text{H}_2\text{O}(g) + \text{CO}_2(g) = \text{Na}_2\text{CO}_3(l) + \text{H}_2\text{S}(g) \quad (3)
\]

Based on the predicted flows in Figure 4, the model under predicts CO₂ by 0.1-0.15 kmol/hr for BL OPs since their predicted equilibrium temperatures are significantly lower than the ones for the blends. Moreover, a very small amount of CO in the range 0.04-0.05 kmol/hr was also absorbed by GL to form formate. Lastly, the final composition of syngas is principally set by the water-gas shift reaction, not included in the model, which continues for an unknown distance into the quench tube and effects all three major components. As the temperature of the syngas fall due to radiative cooling, the equilibrium of the reaction favours the production of CO₂ and H₂ at the expense of CO and H₂O.
Figure 4. A comparison of the change in the experimentally determined (hollow) and predicted (solid) flow rates of H$_2$S with equilibrium temperature for BL (diamond and square) and PO (triangle and circle) OPs.

Up until now, the discussion has focused on characterizing and quantifying the various factors not included in the reactor model but which nonetheless effect the final syngas composition. However, it is instructive to compare the measured carbon flows in syngas with both uncorrected predicted flows and predicted flows that are corrected for the absorption of CO and CO$_2$ in GL and the reaction of CO$_2$ with alkali hydroxides. The results of this comparison are presented in Figure 5 and they reveal two important facts. First, the disagreement between the experimental and the uncorrected flow rates is

Figure 5. A comparison between the experimental (solid diamond) and predicted (hollow) flows rates of carbon in syngas for both the uncorrected (circle) and corrected (triangle) cases. The corrected case takes into account the absorption of CO and CO$_2$ in GL and the reaction of CO$_2$ with alkali hydroxides to form alkali carbonates.
limited to ~ 0.5 kmol/hr at all the OPs. Significantly, it is not systematically affected by blend ratio. This difference equates to between 3-5% of the total carbon input for both pure BL and the blends. It is thus in the same range as the discrepancy in the experimental carbon balance over the gasifier (see Paper II). Second, an adjustment of the predicted flows to take into account reactions and interactions during cooling reduces the difference between the experimental and the predicted values to ~ 0.2 kmol/hr or around 1% of the total carbon input. This high degree of carbon balance closure also allows the estimation of the aforementioned shift between CO and CO₂ with a reasonable level of accuracy.

The above analysis reveals the need to be mindful of the importance of fuel composition in TEC modelling of entrained-flow gasification. However, provided due care is to taken to ensure the use of accurate fuel composition data, unconstrained TEMs can serve as a robust and useful tool for simulating catalytic entrained-flow gasification of a range of biomass-black liquor blends. It is important to note that the thermodynamic model predicts the gasification reactor exit composition, which is different from the cold syngas and green liquor compositions due to the processes occurring in the quench as discussed above.

### 3.3. Green Liquor

The measured flows of total sulfur in GL are compared with the predicted flows of sulfur in smelt for both BL and the blends in Figure 6. The two parameters had previously agreed reasonably well in a study that evaluated two independent datasets.[24] In the present instance, the pure black liquor OPs were underpredicted by the model in all instances, which was expected, given the over prediction of sulfur released as H₂S for these OPs.

![Figure 6](image-url)

Figure 6. A comparison of measured (solid) sulfur flows in green liquor with the predicted (hollow) flows of sulfur in smelt for both BL (circle) and the blends (squares).

Since the agreement between the predicted and measured H₂S flows was good for the blends due to reasons discussed in previous section, the measured GL sulfur flows and the predicted smelt sulfur
flows also showed reasonably good agreement. Seeing as the model over predicted the amount of syngas sulfur by a factor of two for the BL OPs, there is a strong argument for the use of a suitable kinetic expression. However, the acquisition of relevant data such as heating rates and droplet sizes representative of pilot-scale or commercial-scale operation remains problematic. Moreover, the presence of significant amounts of sulfur in syngas is specific to BL or blends thereof, which remain niche fuels. Hence, the inaccurate prediction of H$_2$S yields by equilibrium models is not a major cause of concern for catalytic entrained-flow biomass gasification in general.

A like-for-like comparison between the predicted and measured carbonate concentrations (not shown) revealed that the model consistently over predicted the amount of carbonate formed. Meanwhile, a comparison of the measured GL total inorganic carbon (TIC) flows and the predicted carbonate flows, which is presented in Figure 7 displayed the opposite trend independent of blend ratio. This is because the total inorganic carbon comprises both measured carbonate, which includes the CO$_2$ absorbed by GL and bicarbonate, which is formed by the reaction of CO$_2$ with the alkali hydroxides, as discussed in the previous section. However, the agreement between the predicted and the measured flows improves significantly if the former are adjusted to account for the above, as indicated on Figure 7.

![Figure 7](image.png)

**Figure 7.** A comparison of the measured (solid) total inorganic carbon flow in green liquor and the predicted (hollow) carbonate flow in smelt at reactor exit for both pure black liquor (diamond) and the blends (square). The plus symbols showed the predicted GL flows that have been adjusted to take into account the absorption of CO$_2$ during cooling and quenching to form carbonates and bicarbonates.

### 3.4. Selection of Empirical Correlation for Prediction of HHV

The dataset presented in Table 2 was used to select the most appropriate elemental analysis-based empirical correlation for the estimation of fuel heating value in the model. On the whole, it can be seen quite clearly from Figure 8 that the predictions from the two correlations that explicitly take into account fuel ash content (Channiwala and Parikh, IGT) are in closer agreement with the experimental data compared to the rest (Garcia et al., Sheng and Azevedo). The predicted higher heating values of
only three out of the sixteen fuels evaluated, a kraft black liquor, a hemicellulose sample and a flash pyrolysis oil, fell outside the ±5% band with both IGT and Channiwala and Parikh. Meanwhile, the non-ash containing correlations either under predicted or over predicted the HHVs of more than 35% of the fuels assessed, including two of the impregnated biomass samples by more than 5%.

Figure 8. Comparison of measured and estimated higher heating values of seventeen biomass-based feedstocks. The estimations were obtained using four different elemental composition based empirical correlations derived by Garcia et al. [36] (diamond), Sheng and Azevedo [38] (circle), Channiwala and Parikh [40] (square) and IGT [39] (triangle, solid). The lines represent perfect agreement (solid) and ±5/-5% (dotted).

Given the results in Figure 8, the ash-containing correlations performed significantly better and either of them may be used in the model with little loss in prediction accuracy. However, a decision was made to use the correlation developed by IGT, since it had a slightly better $R^2$ value of 0.96 compared with 0.94 for Channiwala and Parikh and yielded marginally better results for the majority of data points.
3.5. Thermodynamic Equilibrium Modelling of Catalytic Entrained-Flow Biomass Gasification

The predicted HHVs of some selected biomass fuels representing different types and compositions are plotted on Figure 9 in terms of their H/C, O/C and Na/C ratios. As expected, the HHVs decreased with increasing alkali and oxygen contents and increased with increasing H/C ratio. The graph also shows the decrease in HHVs associated with the addition of alkali to biomass, which illustrates the benefit of keeping the alkali/C ratio as low as possible.

Nearly all the fuel mixes simulated reached complete carbon conversion according to equilibrium at the chosen temperature of 1050°C and the oxygen supply associated with this. The exceptions were compositions with a H/C ratio of 1.2, an O/C ratio of 0.4 and alkali/C ratios in the range 0.01-0.2.

3.5.1. External Oxygen Demand

As noted earlier, the model calculates the added oxygen need to reach the specified equilibrium temperature of 1050 °C. The external oxygen demand per unit CO+H₂ (EOD) decreased with increasing H/C ratio, and it was significantly higher for the solids biomass case than for the liquid biomass case. The latter result is somewhat counter-intuitive since the liquid biomass contains more water ballast, but is explained by the fact that this water acts as a gasification agent in the process, leading to a decreased demand of externally supplied oxygen.

It is evident from Figure 10 that the external oxygen demand per unit CO+H₂ was almost wholly a function of the alkali/C ratio for the solid biomass case, particularly at low O/C ratios. This is because an increase in the alkali/C ratio demands more oxygen than is available in the fuel to heat the increasing amounts of alkali to reactor temperature, which causes an increase in the external oxygen demand. The additional alkali also reacts with the CO₂ produced to form alkali carbonate salts, which further pushes the equilibrium towards the conversion of CO to CO₂. The over result is an increase in EOD. Note that this also has the effect of increasing the λ value (not shown). EOD showed a weaker increase with the O/C ratio as the increasing amount of oxygen in the fuel itself was able to meet the oxidant demand.

For the liquid biomass case, EOD increased with both increasing alkali/C ratio and O/C ratio. The cause of this can be seen clearly from a comparison of the differences between the HHVs and the EOD values of 50/50 PO/BL and 0.5M Na₂CO₃ in Figures 9 and 10. While the HHVs of these two fuels differ by ~ 15%, the EOD values show a much greater difference of over 30%. In general, while the λ value was more strongly correlated to changes in the O/C ratio due to being affected by the resulting variations in the stoichiometric oxygen demand, EOD was significantly more sensitive to variations in the Na/C ratio.
Figure 9. The high heating values of the simulated data points on a lower heating value (wet) basis over the full range of O/C and Na/C ratios analysed in the study at H/C ratios of 1.2, 1.5 and 1.8 and fuel solids fractions of 0.75 and 0.95. Selected fuels are marked on the plots for illustration and ease of comparison.
3.5.2. Cold Gas Efficiency

Cold Gas Efficiencies (CGEs) were calculated on a LHV (wet) basis and showed a strong negative correlation with EOD. The highest efficiencies were achieved with carbon-rich and relatively hydrogen-poor compositions that attained complete carbon conversion.
Figure 11. The cold gas efficiencies of the simulated data points on a lower heating value (wet) basis over the full range of O/C and Na/C ratios analysed in the study at H/C ratios of 1.2, 1.5 and 1.8 and fuel solids fractions of 0.75 and 0.95. Selected fuels are marked on the plots for illustration and ease of comparison.

As discussed earlier, some compositions, principally those with the lowest O/C, H/C and alkali/C ratios did not reach complete carbon conversion. This is evident from the bends in the bottom right plots, which show that in certain cases CGE increased with increasing O/C ratio until all the carbon in the fuel had been oxidised. These observations indicate that fuels such as lignin that have low oxygen to carbon and hydrogen to carbon ratios need greater amounts of added oxygen to reach complete carbon conversion, since the oxygen required to reach the specified temperature is not sufficient to reach full equilibrium carbon conversion even if the required amount of alkali were added to speed up the kinetics.
Changes in the H/C had only a limited effect on CGEs as shown in Figure 11. For the solid case, cellulose (H/C = 1.8, O/C = 0.85) and pine woodchips (H/C = 1.5, O/C = 0.67) differed by only 2%-points and this was due to differences in the O/C, and not the H/C; ratio. Fuel moisture content had a notable effect on CGEs. It can be seen from Figure 11 that the CGEs for the wet fuels were ~ 6%-points lower than those for the solids fuels. The energy penalty for liquid feeding is thus similar in scale to that incurred by the addition of an alkali amount to solid biomass that yields an alkali/C ratio of around 0.25.

3.5.3. \( \text{H}_2/\text{CO} \) Ratio in Syngas

There was a striking difference in the \( \text{H}_2/\text{CO} \) ratios of the liquid and solid cases (Figure 12). Compared to the former, the latter returned values that were lower by at least a factor of one-third. Consequently, while the CGE of 50/50 PO/BL was ~ 6% lower than that of the biomass sample impregnated using 1M NaOH, the \( \text{H}_2/\text{CO} \) ratio was more than 40% higher, which translates into a significantly lower load for the shift reactor in a methanol synthesis application. The production of \( \text{H}_2 \) is thermodynamically favourable at high moisture contents due to the water gas shift reaction, which is also supported by the fact that compared to the liquid cases, the solid cases contained significantly greater amounts of CO\(_2\) (not shown).

It appears from looking at the orientation of the contours in the left plots on Figure 12 that for the liquid case, the \( \text{H}_2/\text{CO} \) ratio was nearly insensitive to changes in the O/C ratio. On the other hand, it increased sharply with increasing alkali/C ratio and thus with added oxygen. This may be explained by the oxidation of CO to heat the increasing amounts of alkali, even as the \( \text{H}_2 \) fraction remained relatively stable. Overall, the \( \text{H}_2/\text{CO} \) ratio was rather sensitive to all the parameters that were varied, which served to underscore the difficulty of combining feedstock flexibility with the minimization of downstream shift reactions in the design of a solid-biomass gasification process.
Figure 12. The H₂/CO ratios in cold raw syngas over the full range of O/C and Na/C ratios analysed in the study at H/C ratios of 1.2, 1.5 and 1.8 and fuel solids fractions of 0.75 and 0.95. Selected fuels are marked on the plots for illustration and ease of comparison.

4. Conclusions

The validation of the thermodynamic equilibrium model with data from co-gasification of black liquor and pyrolysis oil demonstrated that TECs may be used to predict the composition of the major components in cold syngas from alkali-catalysed biomass blends to a high degree of accuracy, which is further improved by taking into account reactions and interactions that take place during syngas cooling. This was found to hold true even when the predicted temperature differed from the measured values by over 170°C owing to the probable presence of errors in the composition of pyrolysis oil. There was so little methane in the syngas that the difference between predicted and measured...
temperatures and flows due to its mispredictions was significantly lower than the deviations in experimental carbon balance closure.

The results from the generic thermodynamic equilibrium calculations show that catalytic entrained-flow gasification of biomass-based fuels with O/C ratios in the range 0.5-1 and H/C ratios in the range 1-2 is thermodynamically feasible at a temperature of 1050°C with complete carbon conversion. Elemental composition based empirical correlations which took into account fuel ash content provided significantly better predictions of the HHVs of alkali containing biomass samples.

In order to maximise process efficiency, the alkali/C ratios in impregnated fuels need to be kept at a level that enables the realisation of the catalytic effect without burdening the fuel with unnecessary ballast. The generic simulations showed that best energy efficiencies were returned by solid biomass feedstocks with low H/C and O/C ratios and no more alkali than is required to realise the catalytic effect. However, feedstocks with such compositions also produce syngas with a H2/CO ratio that is sub-optimal for upgrading to biofuels and requires large shift loads. Furthermore, technological developments in entrained-flow gasification of liquid biomass-based feedstocks have far outpaced the development of solid entrained-flow gasification. These factors need to be borne in mind, and if possible taken into consideration while comparing and evaluating fuels on the basis of their energy efficiency and thermodynamic characteristics.

The quantification of gasification performance in terms of the elemental ratios of feedstocks provides an efficient means of comparing fuels and estimating differences in potentially interesting parameters such as cold gas efficiency, external oxygen costs and shift loads. Further work is required to demonstrate and study catalytic entrained-flow gasification of both liquid and solid fuels in both lab and pilot-scale to generate representative data for improved kinetic and techno-economic modelling.
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models of black liquor gasification – influence of minor gas components on temperature, gas
Thermodynamic Equilibrium Modelling of Catalytic Entrained-Flow Gasification of Biomass

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A1 Predicted Equilibrium Temperatures for Pure Black Liquor and Pyrolysis Oil

Figure A1. A comparison of the predicted equilibrium temperatures with an averaged measurement (hollow) from both (a) the top array and (b) the middle of thermocouples in the gasifier for pure black liquor (hollow) and the blends (solid).

It was shown in a comparison of predicted temperature with the readings from the thermocouple located at the bottom that compared with experimental data that the predicted temperature of the BL/PO blends increased significantly with increasing blend ratio. As visible on Figure A1, the same trend was also captured in a comparison of the predicted temperatures with the temperature measurements for the thermocouple arrays located in the middle and near the top of the reactor. Additionally, not only was the divergence between the predicted and measured values also visible for both the 15% PO “cold” and “hot” OPs, but it appeared to increase with increasing reactor temperature.
A1 Elemental Composition of the Dataset Used for Selection of Empirical Correlation for Heating Value Prediction

Table 1. Compositions of the fuels in the experimental dataset used for the selection of the most appropriate correlation for heating value prediction.

<table>
<thead>
<tr>
<th></th>
<th>C [wt%]</th>
<th>H [wt%]</th>
<th>S [wt%]</th>
<th>Alkali [wt%]</th>
<th>O [wt%]</th>
<th>Ash [%]</th>
<th>Data source</th>
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<tr>
<td>1M NaOH</td>
<td>45.01</td>
<td>5.77</td>
<td>N/A</td>
<td>5.43</td>
<td>43.71</td>
<td>N/A</td>
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<td>0.5M Na₂CO₃</td>
<td>47.75</td>
<td>6.25</td>
<td>N/A</td>
<td>1.74</td>
<td>44.59</td>
<td>N/A</td>
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<td>0.1M NaOH</td>
<td>48.36</td>
<td>6.34</td>
<td>N/A</td>
<td>1.00</td>
<td>44.23</td>
<td>N/A</td>
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<td>0.05M K₂CO₃</td>
<td>48.72</td>
<td>6.39</td>
<td>N/A</td>
<td>0.85</td>
<td>44.10</td>
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<td>Saw Dust</td>
<td>47.13</td>
<td>5.86</td>
<td>0.16</td>
<td>N/A</td>
<td>40.35</td>
<td>5.83</td>
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<td>Oak Bark</td>
<td>49.7</td>
<td>5.40</td>
<td>0.1</td>
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<td>39.33</td>
<td>5.3</td>
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<td>Bagasse</td>
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<td>0.01</td>
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<td>0</td>
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<td>Pine Wood</td>
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<td>N/A</td>
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<tr>
<td>Kraft black liquor</td>
<td>29.6</td>
<td>3.60</td>
<td>5.8</td>
<td>29.78</td>
<td>30.9</td>
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<td>29.2</td>
<td>3.99</td>
<td>4.9</td>
<td>25.1</td>
<td>31.1</td>
<td>40.1 SP*</td>
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<td>Flash pyrolysis oil</td>
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<td>6.38</td>
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<td>N/A</td>
<td>37.97</td>
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<td>N/A</td>
<td>41.51</td>
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<td>6.1</td>
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<td>N/A</td>
<td>54.0</td>
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<td>N/A</td>
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<td>Kraft lignin</td>
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<td>N/A</td>
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<td>Organosolv lignin</td>
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<td>N/A</td>
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<td>1.6 Phyliss ECN No. 944</td>
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*SP Technical Research Institute of Sweden; VTT Research Institute of Finland.