Large Scale Experiments and Modeling of Black Liquor Gasification

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Abstract

Biomass gasification could provide a basis for increased electricity and engine fuel production from a renewable source in the pulp and paper industry. This work focuses on the largest byproduct available at the pulp mills, black liquor. Black liquor is a mixture of spent cooking chemicals, dissolved lignin, dissolved carbohydrates and a small portion of inorganic compounds found in the wood. The conventional technology to recover the cooking chemicals and the chemical energy as heat is combustion in large boilers. Here, gasification could be an alternative, replacing or complementing the boilers. The gasification technology produces a combustible gas that can be cleaned to produce electricity in a gas turbine/engine or, be synthesized into valuable chemicals or liquid engine fuels. The technology has been demonstrated in development scale since 2005 and appears to be promising. Still, commercial plants have not yet been built. This thesis focuses on the understanding of the oxygen blown, pressurized, entrained flow, black liquor gasification technology. The main goals have been to increase the understanding about the dominating mechanisms in black liquor gasification and to develop an engineering tool that can be used to design and optimize, pressurized, entrained flow, black liquor gasifiers. To accomplish these goals gas samples were extracted from the gasification reactor using a gas sampling probe that was developed within this work. Gas samples were also collected downstream the quench located underneath the reactor and the results were compared. Finally, an existing numerical model was developed so it can predict the behavior of the black liquor gasifier within reasonable accuracy.

Even though the actual mechanisms in the reactor and quench are very complex it appears that they can be described with relatively simple global mechanisms. The main gas components are dictated by the water gas shift reaction. At the outlet of the reactor the gas composition is not in global thermodynamic equilibrium. However, the main gas components are close to partial equilibrium whilst CH\textsubscript{4} and H\textsubscript{2}S are not. Very little of the available CH\textsubscript{4} is reformed outside the flame region and the primary consumption occurs in the flame through oxidation and reformation. When the system pressure is increased, H\textsubscript{2}S concentration in the gas will increase, the same will happen if the oxygen-fuel ratio is decreased. In the quench, the primary spray flow rate/load (mass flow of black liquor and oxygen) ratio has a critical value of about 0.6 below which the gas concentration of CO\textsubscript{2}, CO, and H\textsubscript{2}, is significantly changed. The H\textsubscript{2}/CO ratio can be changed from about 1.15 to 1.4 by changing the primary spray flow rate/load ratio. The mechanism is associated with the water gas shift reaction and the quenching rate of the gas stream. The computational fluid dynamics reactor model predicts most of the trends when operating conditions are changed and is in good agreement with the experimental results with respect to gas composition and char carbon conversion.
Acknowledgments

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My co-workers at ETC are acknowledged for making ETC an excellent workplace. Kristiina lisa at NREL in Golden Colorado is acknowledged for making my stay at NREL both memorable and interesting. Finally, I which to thank my sisters Anna and Sara and my parents Göran and Marita for supporting me over the years.

Per Carlsson
Piteå, Sweden 3 May 2011
**Contribution of the author**

**Paper I**

Carlsson and Wiinikka planned the experiments. Wiinikka designed the system together with Granberg, Löfström and Lindblom. Wiinikka evaluated the results in cooperation with Carlsson. Carlsson wrote the sections regarding probe tip design, CFD and cooling performance. Wiinikka wrote the sections regarding system design.

**Paper II**

Carlsson wrote the paper and evaluated the results in cooperation with Wiinikka under the supervision of Marklund and Gebart. Carlsson and Wiinikka planned the experiments. Carlsson performed the experiments together with the coauthors.

**Paper III**

Wiinikka wrote the paper and evaluated the results in cooperation with Carlsson under the supervision of Marklund and Gebart. Wiinikka and Carlsson planned the experiments. Carlsson performed the experiments together with the coauthors.

**Paper IV**

Carlsson performed all calculations and wrote the majority of the paper with assistance from Marklund, Furusjö wrote the section regarding the thermodynamic equilibrium calculations. Wiinikka and Gebart supervised.

**Paper V**
Carlsson P., Isa K., Gebart R., Predicting the outlet gas composition from a black liquor gasifier using CFD – Comparison with experiments. Submitted to Energy & Fuels

Carlsson performed all calculations and wrote the paper with assistance from Isa under the supervision of Gebart.
Related non appended papers


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1 Introduction

Gasification is combustion of a fuel using less oxygen than would be required to fully combust the fuel to CO₂ and/or H₂O. Instead, due to the elevated temperature the fuel reacts with O₂, CO₂ and H₂O and forms a flammable gas. The composition of the flammable gas is determined by the fuel, the pressure, the temperature, the residence time and several other parameters and can consist of CO, CO₂, H₂O, H₂, CH₄, C₂H₂, C₂H₄, H₂S, COS and numerous other components.

Commercial gasification started in the beginning of the 19ᵗʰ century [1] with the introduction of gas illumination [2], where the gas was derived from gasified coal. Later, the gas would also be used for cooking and heating purposes. Gas illumination would be surpassed by electricity but in the beginning of the 20ᵗʰ century the interest was turned towards gasification once more. Ammonia synthesis was discovered in the beginning of the 20ᵗʰ century [3] and from ammonia came fertilizers, explosives, urea and other chemicals. Franz Fischer and Hans Tropsch filed a patent application “Process for the production of paraffin-hydrocarbons with more than one carbon atom” in 1925 [4], which made it possible to produce liquid fuels from CO and H₂. The ammonia synthesis required large amounts of hydrogen which could be produced from gasified coal or steam reformed natural gas. The Fischer-Tropsch process required both H₂ and CO which could be produced via gasification. The mixture of CO and H₂ came to be called synthesis gas, or syngas for short, since it was intended as feedstock for the synthesis plants. Since the beginning of 20ᵗʰ century many more processes for converting syngas have been invented and improved and today there exists numerous processes for converting syngas to methanol, ethanol, gasoline, diesel, formaldehyde, acetic acid just to mention a few [5].

Instead of producing chemicals such as ammonia or methanol it is possible to burn the syngas directly in a gas turbine. The hot exhaust gas from the gas turbine can be used to generate steam and drive a steam turbine. The concept together with gasification is called Integrated Gasification Combined Cycle (IGCC). In principle the fuel to the gasifier can be biomass, coal, petroleum residues, municipal solid waste, but most of the development has been done using coal as a fuel. Compared to a coal fired boiler the benefit with IGCC is primarily higher efficiency [1]. On average, the efficiency (coal to electricity) of the coal fired power plants found in the OECD countries 2003 was about 37 % [6]. In current state of the art coal fired boiler steam turbine plants the efficiency can reach about 45 % [7], [1], in the next generation IGCC plants an efficiency of about 48-50 % [8] is expected. Even though the increase may not seem as impressive (45 % to 48 %) the relative increase is about 7 % and thus represents a significant improvement. Hence, the resulting decrease in fuel cost and CO₂ emissions will be of same order (7 %). Or perhaps even more visual, the large coal fired power plants currently being built in China have a power of about
1000 MW per bank and are placed in banks of four (4x1GW) [6]. Hence, the coal consumption will be about 10 000 tons/day (assuming a heating value of 35 MJ/kg for the coal). A 7 % increase in efficiency would correspond to about 700 tons of coal per day or 250 000 tons per year. As a reference; the total consumption of coal (not including coke) by the Swedish manufacturing industry sector in 2009 was 569 000 tons [9]. The drawback with IGCC compared to a boiler is primarily a higher capital cost caused by lack of standardized plants [10].

1.1 The role of biomass
So far the emphasis has been on coal gasification and the vast majority of the operating gasifiers use coal or petroleum residue as fuel. There is however drawbacks with coal. Apart from the release of heavy metals [11], SOx [12], NOx [13] and ash related issues [14] the estimated global release of CO₂ from burning fossil fuels was in 2007: 8365 million metric tons (on carbon basis). Out of this 3295 Mton was from solid fuels, 3087 Mton was from liquids and 1551 Mton was from gas [15]. Hence, almost 40 % of the CO₂ emitted come from combustion of solids, primarily coal. Reports on shrinking glaciers [16], draughts and floods [17] and the increase in global temperature [18] have become almost daily occurrences. The scientific community has drawn the conclusion that the main reason is the increased level of CO₂ in the atmosphere [19]. Because of these reasons, attention has turned to biomass as fuel for gasifiers. A biomass fueled gasifier could, at least in principle, produce products (together with a synthesis plant or CC) that are completely CO₂ neutral. If engine fuel was produced the net contribution of CO₂ would be zero since the CO₂ formed during combustion (in the engine or turbine) would be the same amount that was stored in the biomass to begin with. The term CO₂ recovery cycle springs to mind (biomass to syngas to fuel to atmosphere to biomass) since the same carbon atoms could be used as energy carriers over and over (ideally). However, the amounts of biomass that would be needed to replace, for example the transportation fuels are large, very large. An estimation based on data from Statistics Sweden [20] and a biomass to liquid efficiency of 50 % shows that it would require 100 000 ton of biomass / day (heating value of biomass, 18 MJ/kg) or 37 Mton per year to replace all gasoline and diesel that is used in Sweden using data from 2009. However, remember that the previously described Chinese coal fired plant handled about 10 000 tons of coal every day so about 10 plants of that size would be required. Still, the amount of biomass is about 60 % of what was logged in Swedish forests in 2004 (61 Mton) [21], so a simultaneous reduction of the usage of gasoline and diesel would be required to make it feasible.
In Sweden, the forest products industry handles about 37 Mton (on dry basis) of biomass per year or about 60% of the total logging in Sweden [21]. Hence, existing industry already handles the amount of biomass that would be necessary to replace all gasoline and diesel in Sweden. It would seem that an optimal location for a biomass fueled gasifier is adjacent to a large pulp or saw mill to take advantage of existing infrastructure and upgrade byproducts or residue to electricity (IGCC), chemicals or engine fuels. If properly integrated, efficiency could be raised, there are economic and environmental benefits, in addition the pulp and saw mills could get an additional product in their line (or increased production of); electricity, chemicals, or engine fuels.

The single largest byproduct (not to be confused with waste product) from a kraft pulp mill is black liquor. When cellulose is extracted from wood chips in the pulp mill digester using a cooking-chemical called white liquor the byproduct is weak black liquor. From the digester the weak black liquor contains about 15% solids. The solids are mainly the spent cooking-chemicals (Na₂S, NaOH, Na₂CO₃, and Na₂SO₄), dissolved lignin, dissolved carbohydrates and a small portion of inorganic compounds found in the wood [22]. The weak black liquor is sent through several evaporation units in order to raise the solids content. The evaporators raise the solids content to about 75% concentrating the weak liquor to black liquor. The black liquor is a highly viscous fluid with a heating value of about 12 MJ/kg (on a dry basis, can be compared to ~45 MJ/kg for crude oil). The alkali cooking chemicals which make up about 1/3 of the mixture result in an elevated pH of about 12-14 [23]. A typical black liquor composition is showed in Table 1 together with coal and softwood (pine) as comparison.

For the pulp mill to be economical the energy available in the black liquor and the spent cooking chemicals need to be recovered. The conventional technology for this is large boilers called recovery or Tomlinson boilers. The black liquor is fired into the recovery boiler using liquor guns which are designed to produce droplets with a diameter of approximately 0.5-5 mm. The droplets dry and partly devolatize (thermal degradation of organic matter) as they fall towards the char bed located at the bottom of the boiler. The use of a coarse spray prevents the particles to be entrained in upward flowing gases thus reducing the amount of fouling and fly ash [22]. The char bed has reducing conditions thus converting Na₂SO₄ to Na₂S through reactions with carbon in the black liquor [22], [24]. The ash (called smelt) is retrieved through smelt spouts and is dissolved in weak white liquor (diluted cooking chemical). Through this step green liquor is formed. By adding burnt lime (CaO) to the green liquor (causticizing), white liquor is formed (which is the active cooking chemical). The spent lime (CaCO₃) is filtered from the white liquor and sent through a large kiln to turn it into burnt lime once again. Hence, the recovery system is a closed loop system and ideally the same chemicals are used over and over again. However, to avoid accumulation of non-process
elements originating from the pulp wood a small amount of material is taken out from the chemical recovery loop and is compensated with the addition of so called make-up chemicals.

Table 1. Proximate and ultimate analysis for typical northern Sweden black liquor [25], bituminous coal [1] and softwood [26].

<table>
<thead>
<tr>
<th>Proximate analysis</th>
<th>Black liquor % wt</th>
<th>Bituminous coal % wt</th>
<th>Wood % wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>24.8</td>
<td>13.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Volatiles</td>
<td>28.9</td>
<td>37.0</td>
<td>79.4</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>9.9</td>
<td>39.3</td>
<td>14.2</td>
</tr>
<tr>
<td>Ash</td>
<td>36.4</td>
<td>10.7</td>
<td>0.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ultimate analysis as dry</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>S</td>
</tr>
<tr>
<td>Na</td>
</tr>
<tr>
<td>K</td>
</tr>
<tr>
<td>HHV MJ/kg</td>
</tr>
</tbody>
</table>
1.2 Black liquor gasification
As with coal gasification versus coal boilers, gasification of black liquor could lead to increased energy efficiency [27] compared to the conventional recovery boiler. In addition, more flexible pulping methods could be adopted which could increase the pulp yield [28], i.e. more pulp per ton biomass. However, compared to a coal fired gasifier the black liquor gasifier have two products; the smelt (and subsequently green liquor) and the syngas. If black liquor is gasified the more important of those two products is the green liquor not the syngas. A poor smelt quality (high char carbon content, poorly reduced Na₂SO₄) leads to an increased cost for the white liquor production and in the end, more expensive paper. The target is therefore to produce a smelt and later on green liquor that is comparable with the one produced from the recovery boiler.

No matter what fuel is to be gasified (coal, petcoke, woody biomass, black liquor etc.) there is one key feature that distinguishes gasification technologies from one another. Either the gasifier is operated well above the melting temperature of the ash (slagging mode) or well below the melting temperature of the ash (non-slagging mode). Close to the melting point, the ash becomes sticky causing plugging, bed agglomeration (in fluidized bed gasifiers), fouling and so on. The difficulty is that there is seldom a distinct melting temperature rather a temperature range where the ash is soft, sticky or has a high viscosity [29].

There have been several attempts to gasify black liquor. Whitty et al. [30] have written an excellent historical review on the subject identifying some 10 companies that have developed non-slagging black liquor gasifiers and just as many operating in slagging mode. However, there have been obstacles: lack of funding, material related issues and market swings (energy/oil prices) so currently there are only two companies that offer black liquor gasifiers commercially, Chemrec and ThermoChem Recovery International (TRI).

Since 2005 a TRI (non-slagging, indirectly heated steam reformer) gasifier has been in operation in Trenton, Canada using black liquor as fuel. The gasifier has a capacity of 115 ton/day and an accumulated operating time of 23 000 hours [31]. Chemrec has two operating gasifiers; one air blown atmospheric at New Bern, USA (330 ton/day, 47 000 h, startup 1996) and an oxygen blown, entrained flow, pressurized, high temperature gasifier located in Piteå Sweden (20 ton/day, 11 500 h, startup 2005, schematics showed in Figure 1) [32]. This work will focus on the later.
The Chemrec Black Liquor Gasification (BLG) development plant called DP-1 is schematically presented in Figure 1. The main parts of the plant are; a slagging refractory lined entrained-flow gasification reactor (2.3 m in height and 0.6 m in inner diameter) used for direct gasification of the black liquor at about 1050 °C and 30 bar\textsuperscript{1} to produce a raw gas and a liquid smelt; a quench cooler beneath the reactor where the raw gas and smelt are separated from each other and the smelt is dissolved in water forming green liquor; a Counter Current Condenser (CCC) that cools the steam saturated raw gas and condenses the water vapor and any other condensable species that may be present. The heat recovered from the gas condensation may be used to generate low/medium pressure steam that can be used in the pulp and paper process. Even though the development plant is significantly smaller than a commercial unit it is equipped and operated as a commercial unit. Hence, there are several restrictions on operating conditions mainly to prevent fouling and excessive wear on the refractory lining.

DP-1 uses about 1% of the black liquor produced at the adjacent pulp and paper mill Smurfit Kappa Kraftliner (~2000 ton/day). Today a conventional recovery boiler is used to recover the cooking chemicals and the heat. Assuming that the recovery boiler is to be replaced with a black liquor gasifier, how can the capacity of the DP-1 plant be increased from 20 ton/day (3 MW\textsubscript{th}) to 2000 ton/day (300 MW\textsubscript{th})?

\textsuperscript{1} Gauge pressure will be used throughout the thesis
It would be possible to use the existing DP-1 plant as a template and simply make copies, a hundred of them. However, this would neither be economical nor energy efficient. It would be possible to scale the gasifier and burner dimensions with a factor 100, the gasification reactor would then be 230 m tall or about 4 times taller than the recovery boiler. Add to this the burner, the quench and auxiliary equipment. Volume scaling could be used, for example utilize that the power density (MW/m³) should be equal between the small and the large gasifier (300 MWth reactor dimensions about 2.8 m in diameter and 11 m tall). Demands on redundancy might influence the number of gasifiers that are built. For example, if the plant consists of three gasifiers, one could undergo maintenance while the other two cover the capacity. Of course, the gasifiers have to be dimensioned to cover the increased load during maintenance work (3x150 MWth, reactor dimensions about 2.2 m in diameter and 8.6 m tall), or a decrease in production has to be accepted during maintenance work (3x100 MWth, reactor dimensions about 1.9 m in diameter and 7.5 m tall). The rough dimensions of a gasifier can be decided in this way; however it is difficult to judge the performance, for example char conversion, smelt quality, syngas quality, burner performance etc. of the gasifier. Hence, additional information could prove valuable not only when designing the gasification reactor but also downstream and auxiliary equipment such as gas coolers, burners and gas cleaning equipment.

1.3 Thesis objectives and outline
The goal with this thesis is to: i) increase the understanding about the dominating mechanisms in black liquor gasification. ii) Develop an engineering tool that can be used to design and optimize pressurized, entrained flow, black liquor gasifiers. In order to accomplish these objectives the following have been done. A water cooled quench probe was developed in order to collect gas samples from inside the DP-1 gasification reactor. The DP-1 reactor and quench was operated at different process conditions and the influence on the gas composition was evaluated. Finally, an existing numerical model [33] was improved in order to predict the gas composition within reasonable accuracy.
Due to reactions in the quench downstream the gasification reactor in the BLG process it is possible that the gas coming from the quench is not representative of the gas present in the reactor. Since the CFD model (see section 3.1) does not include the quench, it is difficult to make a direct comparison between the computed reactor gas composition and the gas from the quench. It was therefore decided to develop a sampling system that could be used to extract gas from the hot part of the gasification reactor. This section will describe the equipment used for sampling, the main mechanisms in the reactor and quench and the experimental campaigns performed within this thesis work.

2.1 Gas sampling equipment

High temperature, high pressure, high smelt loading and reducing conditions make gas sampling inside the hot part of a black liquor gasifier a challenging task. Severe corrosion issues appear as well as clogging of the sampling probe caused by the high particle loading inside the reactor. In Figure 2, a sketch of the used high temperature gas sampling system can be seen. Since the gas sampling system handles flammable and explosive gases, it was designed in compliance with ATEX [34] [35], IEC 61508, and IEC 61511 directives.

Figure 2. Schematic drawing of the high temperature gas sampling system. Abbreviations: TC (thermocouple), FI (flow indicator), MV (manually operated valve), AV (automatically operated valve), PG (pressure gauge).
The geometry of the gas sampling probe is presented in Figure 3. The probe mainly consists of three concentric pipes (outer, middle and inner) with outer diameters 30 mm, 18 mm and 8 mm, respectively. The wall thicknesses of the three pipes were 2.0 mm (outer), 2.0 mm (middle) and 1.5 mm (inner). Gas samples from the reactor were withdrawn through the inner pipe. At the probe tip an orifice with a diameter of 1.5 mm was formed. The purpose of the orifice is to limit the maximum possible mass flow rate of syngas and also, by creating the largest pressure drop in the gas sampling system close to the probe tip, quench the sample gas by rapid expansion of the syngas downstream the orifice.

The probe, made out of stainless steel (SS-2333) was water cooled to reduce corrosion from direct contact with hot alkali smelt and withstand the reducing conditions inside the reactor. The flow rate of cooling water was estimated from a heat balance calculation taking external convection and radiation from the hot gas and internal convection from the cooling water into account. The heat balance calculation showed that, using water as a cooling medium, a flow rate of more than 20 l/min would be sufficient to give a surface temperature of about 200 °C, which was estimated to be adequate to ensure the structural integrity of the probe. When hot syngas is withdrawn through the probe, the length of the inner pipe will increase due to thermal expansion. To avoid large tensile stresses in the inner pipe the probe was constructed with a 90° bend (see Figure 3). By doing so, the inner pipe can expand up to 9 mm corresponding to about a 900 °C temperature increase, before it is brought in contact with the outer pipe. The corresponding bending moment at the end of the probe where the inner pipe is welded to the outer pipe is for all practical purposes negligible.
2.1.1 Probe tip design
The initial probe sampling tests suffered from rapid clogging of the probe tip orifice. When this occurred the sampling experiment had to be stopped; the process plant shut down, the sampling probe removed, cleaned, and reinstalled; and the plant taken into operation again. All of these steps took approximately 24 hours to perform. Hence, to prevent clogging, the probe tip was redesigned in several stages.

The smelt, which primarily consists of a binary mixture of Na$_2$CO$_3$ and Na$_2$S, has a melting behavior that depends on the smelt mixture composition [36], [37]. Pure Na$_2$CO$_3$ melts at a temperature of 858 °C and pure Na$_2$S at a temperature of 1188 °C. The eutectic point for a binary mixture of Na$_2$CO$_3$ and Na$_2$S is approximately 762 °C and occurs for X$_{Na2S}$ of 0.4.

A flow visualization experiment using a water spray and a vacuum suction pump was conducted in order to get an illustration of the key features of the liquid smelt behavior close to the probe tip during gas sampling. The result then made it possible to redesign the probe tip to prevent clogging during the real experiments. Since the smelt has a viscosity similar to water at high temperature [38] it was believed that by using water as model liquid the real conditions inside the reactor could be properly simulated. The water spray experiments showed that great care and careful consideration is needed in the probe tip design, not only during sampling but also during purging between samples. Some of the tested probe tip configurations performed very well during suction but poorly during purging. This was mainly due to recirculation caused by the anti-clogging probe tip shields. From the water spray experiments it was found that two concentric holes and an anti-clogging probe tip shield with an angled piece shield at the end (see Figure 4) gave good results.
with respect to separation of water from the gas during sampling and possible problems during purging. The anti-clogging shield at the probe tip was designed so that the liquid smelt film formed on the top of the shield would not be convected to the inside of the shield during suction. However, for this to work the probe shield temperature had to be higher than the melting temperature of the smelt.

![Streamlines in the shielded probe tip during purging: Shield length L = 50 mm (upper), shield length L = 100 mm (lower). Flow is from right to left.](image)

If the anti-clogging shield was colder than the liquid smelt film, the film would freeze on the surface and eventually cause clogging. On the other hand, keeping the tip hot would result in rapid corrosion that could destroy the shield in a few hours. This was also confirmed by real high temperature experiments in the gasifier where severe corrosion was seen on the anti-clogging shield. In one of the performed experiment the anti-clogging shield even corroded away completely. However, in these experiments the ability to withdraw gas was uncompromised. It was therefore not possible to determine if the shield was crucial for the design of the probe tip but since the probe showed good performance with the shield mounted, it was kept in the design as an added safety measure. Even though the anti-clogging shield was designed to eliminate the problem of getting smelt film convected into the probe a small fraction of the film still will flow inside the shield, probably due to surface tension effects. This was recognized as one of the mechanisms that may still cause clogging. Even if the rate of entrainment of smelt into the shield is low it will eventually result in a pool of liquid smelt in the anti-clogging shield. The syngas will exert forces on this pool during suction that will force smelt towards the first orifice where it will freeze and cause clogging. Another potential mechanism that could cause clogging is small liquid smelt particles that are entrained by the gas stream. The particles will impact on the surface close to the first orifice where they will freeze and stick to the wall. Since the concentric hole configuration was
chosen for the probe tip, and the experiments had exhibited good particle-gas separation, the aerodynamics in the probe were analyzed with Computational Fluid Dynamics (CFD) using the commercially available finite volume method based software, ANSYS CFX. The calculations were performed in order to confirm the intuitive results about the behavior of the probe tip during suction and when purged with nitrogen.

The simulations also yield information about the quenching effect from expansion of the gas from the reactor pressure to atmospheric pressure. The flow model was fully compressible with gas properties representative of the expected gas mixture in the reactor. Turbulence was modeled using the k-ε turbulence model with scalable wall functions [39], [40]. The boundary conditions (pressure in, pressure out) were set to the measured values during sampling and purging. The walls of the probe were treated as adiabatic. During purging, the length of the anti-clogging shield (L in Figure 4) played an important role; it had to be sufficiently long so that recirculation would not cause a transport of smelt into the shield. As can be seen in Figure 5 when a shorter anti-clogging shield is used, there are three main eddies in the anti-clogging shield; the tip, the upper and the lower eddy. With a longer anti-clogging shield a plug flow at the probe tip is created that suppresses the tip eddy that could potentially entrain and transport smelt into the shield.

![Flow Characteristics](image1.png)

**Figure 6. Flow characteristics at the critical restriction. Flow is from left to right. (upper): Contour plot of Mach number (M) up to M < 0.1. (lower): Contours by temperature, line showing M = 1.**
During suction, the gas was accelerated through the shield, the first orifice and finally through the flow restrictor orifice. The average velocity in the anti-clogging shield was approximately 1.2 m/s corresponding to a Mach number of 1.5E-3 and increased by a factor 50 at the first orifice (see Figure 6). Through the flow restrictor orifice the velocity was increased even further, reaching sonic conditions (M=1), with a strong shock diamond pattern at the exit from the orifice. The rapid expansion in the orifice has an associated rapid temperature drop that will freeze any chemical reactions (see section 4.4 Error estimation and uncertainties). Assuming isentropic expansion, a reactor pressure of 30 bar, a reactor temperature of 1000 °C, a nozzle downstream pressure of 1 bar and a syngas specific heat ratio (Cp/Cv) of 1.25, the gas temperature would be lowered approximately 350 °C due to the expansion. Similar results were seen in the simulations, but even larger local temperatures drops were observed caused by the predicted shockwaves. Since cooling due to wall heat flux was neglected in the CFD simulations the temperature reaches the reactor temperature again after the expansion. Gas sample experiments using the probe in the gasifier has showed that the probe outlet thermocouple (TC-2G, see Figure 2, page 9) never exceeded 90 °C during sampling, implying that the cooling rate is about 10 000 °C/s given the short residence time in the probe (Figure 7).

![Figure 7. Typical behavior of purging nitrogen flow rate (FI-1G), cooling water temperature (TC-2W) and probe temperature (TC-2G) during gas sampling. 1-2: The pressure vessel is purged with nitrogen. 2: The nitrogen is turned off. 3-4: Gas sampling from the reactor. 5: The purging nitrogen is turned on.](image-url)
2.2 Mechanisms in the reactor and quench

Combustion and gasification characteristics of black liquor in lab-scale have been investigated by several authors [41] - [47]. However, to the author’s knowledge, no analyses have been conducted with samples taken inside a gasification reactor of this size or larger. This section will highlight parts from paper II and III that focuses on the influence of operating conditions (in the reactor and the quench) on the gas composition.

In the gasification reactor, pre-heated (140 °C) black liquor is centrally introduced at the reactor top via a gas assisted atomization nozzle producing a fine spray of droplets and ligaments [48]. As the atomized black liquor pass through the gasification reactor, the black liquor undergoes four main stages of conversion [41], [49]: drying, devolatilization, char gasification and smelt formation (see Figure 8).

During the conversion, the morphology of the droplets undergoes a significant change of which swelling is most predominant [45]. The conversion stages for the resulting black liquor droplets mainly occur sequentially, one after another, but may also overlap [50]. During the different conversion stages there is a large net mass transfer from the black liquor to the gas phase. During drying, the contained water in the black liquor is evaporated. During devolatilization, volatile matter (e.g. H₂, CO, H₂S, CO₂, H₂O CₓHᵧOz) is released due to the thermal degradation of the original organic material in the black liquor [41], [42]. The remaining char is then gasified via
reactions involving CO, CO₂, H₂ and H₂O and finally the Na₂SO₄ in the smelt is reduced to Na₂S through reaction with carbon [25]. A summary of the main global reactions are showed in Table 2.

<table>
<thead>
<tr>
<th>NO.</th>
<th>REACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>H₂O(l) → H₂O(g)</td>
</tr>
<tr>
<td>R2</td>
<td>H₂ + ½O₂ → H₂O</td>
</tr>
<tr>
<td>R3</td>
<td>CO + ½O₂ → CO₂</td>
</tr>
<tr>
<td>R4</td>
<td>CH₄ + ½O₂ → CO + 2H₂</td>
</tr>
<tr>
<td>R5</td>
<td>CH₄ + 2O₂ → CO₂ + 2H₂O</td>
</tr>
<tr>
<td>R6</td>
<td>H₂S + O₂ → SO₂ + H₂</td>
</tr>
<tr>
<td>R7</td>
<td>COS + O₂ → SO₂ + CO</td>
</tr>
<tr>
<td>R8</td>
<td>C₄H₁₀O₄ + aO₂ + bH₂ + cH₂O → nCO + mH₂</td>
</tr>
<tr>
<td>R9</td>
<td>CO + H₂O ↔ CO₂ + H₂</td>
</tr>
<tr>
<td>R10</td>
<td>CH₄ + H₂O ↔ CO + 3H₂</td>
</tr>
<tr>
<td>R11</td>
<td>COS + H₂O ↔ CO₂ + H₂S</td>
</tr>
<tr>
<td>R12</td>
<td>SO₂ + 3H₂ ↔ 2H₂O + H₂S</td>
</tr>
<tr>
<td>R13</td>
<td>C + CO₂ ↔ 2CO</td>
</tr>
<tr>
<td>R14</td>
<td>C + H₂O ↔ H₂ + CO</td>
</tr>
<tr>
<td>R15</td>
<td>C + 2H₂ ↔ CH₄</td>
</tr>
<tr>
<td>R16</td>
<td>C + O₂ ↔ CO₂</td>
</tr>
<tr>
<td>R17</td>
<td>C + ½O₂ ↔ CO</td>
</tr>
<tr>
<td>R18</td>
<td>C + ½Na₂SO₄(l) ↔ ½Na₂S + CO₂</td>
</tr>
<tr>
<td>R19</td>
<td>2NaOH(l) + CO₂ ↔ Na₂CO₃(l) + H₂O</td>
</tr>
<tr>
<td>R20</td>
<td>Na₂S(l) + H₂O + CO₂ ↔ Na₂CO₃(l) + H₂S</td>
</tr>
<tr>
<td>R21</td>
<td>Na₂S(l) + 2CO₂ ↔ Na₂CO₃(l) + COS</td>
</tr>
</tbody>
</table>

The rapid gas phase reactions involving oxygen (R2) – (R7) take place close to the burner since the sub-stoichiometric amount of supplied oxygen will be consumed very quickly when it enters the hot and reactive gas atmosphere inside the reactor. Because of this, mass transfer limited heterogeneous reactions with oxygen, (R16) and (R17) only occur to a very small degree. Reaction (R8) represent the degradation of heavier hydrocarbons; the formation and degradation of these compounds (typically tars) is complex and will not be discussed in detail in this work. The water gas shift reaction (R9) is believed to be the determining reaction for the bulk gas composition (H₂O, H₂, CO₂ and CO). Because of recirculation of gas from the lower part of the reactor to the top, H₂S and COS may be oxidized to SO₂ close to the burner where oxygen is present. However, in the post flame region reaction (R6) and (R7) are most probably equilibrated by (R12) and (R11) thus, converting SO₂ back to H₂S and COS given the reducing conditions [51]. The heterogeneous gasification reactions (R13) - (R15) take place in the absence of oxygen in the post flame region and possibly on the walls of the reactor where some of the droplets may impact, these together with
the reduction of Na₂SO₄ (R18) converts most of the fixed carbon in the resulting black liquor char. The dominating reactions for the smelt formation are believed to be reactions (R19) - (R21).

In general, gas from a gasification reactor is contaminated with various components that must be removed before the gas can be used in a synthesis process or for power production [1]. These contaminants may be particulates (soot or inorganic ash particles), tars and compounds of sulphur and chlorine. All such removal processes operate at a temperature considerably lower than that of the gasifier itself [1]. Therefore, the gas has to be cooled several hundred degrees. One method to cool the gas during slagging gasification is to introduce fine water droplets into the hot gas and thus quench the conversion products by evaporation of the water. Another important aspect is to prevent that the ash deposits on cooled surfaces in the quench. In contrast to ordinary gasification processes, the ash product from the black liquor gasifier (smelt dissolved in water forming green liquor in the quench) is an important product from the gasifier that must be recycled to the pulp mill.

The general principle of the quench in the current type of gasifier was first proposed by Stigsson and Bernard [52] (see Figure 9). The hot product gas with smelt droplets from the reactor is forced to pass through the reactor throat and down into the quench tube. At the entrance of the quench tube, cooling liquid (water or condensate from the counter current condenser) is injected into the gas flow through nozzles (primary spray). The gas is then cooled by evaporation of the primary spray to a predetermined temperature greater than the steam saturation temperature at the prevailing quench vessel pressure, to provide a gas containing superheated steam. The gas with its superheated steam is then forced to change direction and turn about 180° at the lower end of the quench tube. The gas then flows upwards and out of the outer surrounding tube concentrically arranged around the central quench tube. The entrained particles, containing inorganic alkaline compounds, are forced by gravity and inertia to fall into the quench pool where the compounds are dissolved in water to form green liquor. The separated gas (with superheated steam) is then further cooled by a second cooling liquid (secondary spray) and finally bubbled through a water column before it leaves the quench vessel. The gas has now been cooled down to the steam saturation temperature at the prevailing quench vessel temperature. The level of the liquid in the quench pool is an operational parameter, which can be controlled by addition of cooling liquids and by withdrawal of green liquor.
The hot gas at the outlet of the reactor mainly consists of H₂, CO, H₂O, CO₂, CH₄, H₂S, and COS. A typical gas composition (as dry and nitrogen free, mol basis) before cooling is 34 % CO₂, 29 % CO, 34 % H₂, 1.5 % CH₄, 1.5 % H₂S and 500 ppm COS. When the temperature in the top of the quench is reduced due to the evaporation of water from the primary spray, the composition of the gas may be changed either by the water gas shift reaction (Q1 in Table 3), the hydrogenation reaction (Q2) or the hydrolysis reaction (Q3) [1]. The hydrogenation reaction (Q2) and the hydrolysis reaction (Q3) control the relation between the H₂S and COS. The smelt and the product gas may also interact in the quench with water (in vapor or liquid phase) according to reactions Q4-Q14. Reaction Q4 describes the formation of Na₂CO₃ and H₂S from Na₂S, H₂O and CO₂. Reactions Q5-Q7 describes the dissolution of smelt in the quench pool or in the water droplets. The product is an aqueous solution of Na⁺, OH⁻, HS⁻, and CO₃²⁻ ions, which make up the green liquor. CO₂ and H₂S may be absorbed in the water droplets or in the green liquor through reaction Q8 and Q9. Reactions Q10-Q12 describes the interaction of absorbed CO₂ and H₂S with the negative ions in the green liquor. Finally, reaction Q13 and Q14 describe the formation and destruction of HCO₃⁻.

²Reaction Q1 and Q3 are identical to reaction R9 and R11, in Table 2. Dominating global reaction in the reactor have a lead entry with R and in the quench Q. To emphasize that some reactions occur both in the quench and in the reactor they are mentioned twice.
Table 3. Main global reactions in the black liquor gasification quench

<table>
<thead>
<tr>
<th>NO.</th>
<th>REACTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q1</td>
<td>CO(g) + H₂O(g) ⇌ CO₂(g) + H₂(g)</td>
</tr>
<tr>
<td>Q2</td>
<td>COS(g) + H₂(g) ⇌ CO₂(g) + H₂S(g)</td>
</tr>
<tr>
<td>Q3</td>
<td>COS(g) + H₂O(g) ⇌ CO₂(g) + H₂S(g)</td>
</tr>
<tr>
<td>Q4</td>
<td>Na₂S(s) + H₂O(l) + CO₂(g) ⇌ Na₂CO₃(s) + H₂S(g)</td>
</tr>
<tr>
<td>Q5</td>
<td>NaOH(s) ⇌ Na⁺(aq) + OH⁻(aq)</td>
</tr>
<tr>
<td>Q6</td>
<td>Na₂S(s) ⇌ 2Na⁺(aq) + HS⁻(aq) + OH⁻(aq)</td>
</tr>
<tr>
<td>Q7</td>
<td>Na₂CO₃(s) ⇌ 2Na⁺(aq) + CO₃²⁻(aq)</td>
</tr>
<tr>
<td>Q8</td>
<td>CO₂(g) ⇌ CO₂(aq)</td>
</tr>
<tr>
<td>Q9</td>
<td>H₂S(g) ⇌ H₂S(aq)</td>
</tr>
<tr>
<td>Q10</td>
<td>2OH⁻(aq) + CO₂(aq) ⇌ CO₃²⁻(aq) + H₂O(l)</td>
</tr>
<tr>
<td>Q11</td>
<td>OH⁻(aq) + H₂S(aq) ⇌ HS⁻(aq) + H₂O(l)</td>
</tr>
<tr>
<td>Q12</td>
<td>2HS⁻(aq) + CO₂(aq) ⇌ CO₃²⁻(aq) + H₂S(aq)</td>
</tr>
<tr>
<td>Q13</td>
<td>CO₃²⁻(aq) + H₂O(l) + CO₂(aq) ⇌ 2HCO₃⁻(aq)</td>
</tr>
<tr>
<td>Q14</td>
<td>HCO₃⁻(aq) + OH⁻(aq) ⇌ CO₃²⁻(aq) + H₂O(l)</td>
</tr>
</tbody>
</table>

As discussed by Stigsson and Bernard [52], when hot CO₂ containing gas is brought in contact with an alkaline solution, CO₂ tends to be absorbed into the solution and the resulting pH level in the green liquor is thereby lowered. If too much CO₂ is absorbed in the green liquor HCO₃⁻ will be formed according to reaction Q13. This is, an undesirable compound in green liquor, since it increases the load on the causticizing system where sodium hydroxide is regenerated from the sodium carbonate in the green liquor. The formation of HCO₃⁻ in the green liquor can be minimized by cooling the hot gas in multiple stages in the quench and by separating the inorganic alkaline compounds from the hot gas at an intermediate temperature before the hot gas is cooled to the saturation temperature at the prevailing quench vessel pressure. Therefore, the gas is cooled by two different water sprays (primary and secondary) in the quench (see Figure 9). The flow rates in these sprays can be controlled independently.

2.3 Variation of operating conditions

During the experimental campaign several different process parameters were varied both in the reactor and the quench. These variations resulted in variations in operating conditions such as pressure, temperature, gas residence time, quench cooling performance etc. Before the experimental campaign a base operating condition was established at 27 bar and a process temperature of about 1050 °C, for which the liquor composition (showed in Table 4) used in the experiments corresponded to an equivalence ratio (defined as \( \lambda = (x_{O₂}/x_{fuel})/(x_{O₂,stoich}/x_{fuel,stoich}) \), where x is mol fraction) of 0.434.
Table 4. Composition of the black liquor used in the experiments, higher heating value (HHV) is on dry basis

<table>
<thead>
<tr>
<th>ULTIMATE ANALYSIS (dry solids)</th>
<th>%wt</th>
<th>Relative uncertainty %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>31.3</td>
<td>2.0</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
<td>6.0</td>
</tr>
<tr>
<td>O</td>
<td>37.2 *</td>
<td>9.1 **</td>
</tr>
<tr>
<td>N</td>
<td>0.1</td>
<td>20.0</td>
</tr>
<tr>
<td>S</td>
<td>5.6</td>
<td>13.0</td>
</tr>
<tr>
<td>Na</td>
<td>20.1</td>
<td>8.0</td>
</tr>
<tr>
<td>K</td>
<td>2.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Cl</td>
<td>0.1</td>
<td>13.0</td>
</tr>
</tbody>
</table>

PROXIMATE ANALYSIS

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>24.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Volatiles</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>HHV MJ/kg</td>
<td>12.57</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*by difference, **by difference from uncertainties in participating elements using extremes

In the reactor, the process conditions; pressure, temperature, residence time and level of atomization was affected by varying the operational parameters; pressure, equivalence ratio, black liquor mass flow rate and black liquor pre-heating temperature. In the quench, the cooling rate was affected by varying the primary and secondary spray flow rate. The performed variations are described thoroughly in paper II and III. Here, the emphasis will be on variations in pressure, equivalence ratio, black liquor mass flow rate and primary spray. The goal with the variations was to increase the understanding about the global mechanisms in the reactor and quench and also, obtain data that could be compared to the results from the CFD model described in section 3.1.

The probe was installed in the lower part of the gasification reactor approximately 0.6 m above the outlet (approximate position in Figure 8 on page 15) before the start of the gasification process. When the gasification process was stable, determined by monitoring the process control sensors, a gas sample from the reactor was taken. At the same time, syngas was collected after the gas cooler into a Tedlar bag so a comparison could be made between the gas composition in the reactor and the one after the quench. The gas samples, both from the reactor and from the gas cooler, were then analyzed with respect to CH₄, CO, CO₂, H₂, N₂, H₂S, COS, and O₂/Ar using a Varian CP-3800 gas chromatograph.

The effect of reactor pressure was investigated by running the DP-1 plant at three different pressures: 15, 20 and 27 bar (called, -P, 0P and +P in Table 5). During the experiments the temperature inside the reactor was held constant at around 1050 °C by changing the equivalence ratio from approximately 0.43 to 0.46. Since the wall heat losses (estimated to approximately 90kW) will be a greater portion of the total thermal throughput at reduced pressure (and
consequently reduced black liquor flow rate), the equivalence ratio was increased slightly at reduced pressure in order to maintain a constant reactor temperature.

As can be seen in Table 5 the base operating condition described earlier can be found in the high pressure case (+P) and in the medium temperature case (0°C). The normalized gas residence time showed in Table 5 is based on a plug flow assumption, with the base operating conditions set to unity. In this case, high pressure in combination with low mass flow rates results in a long gas residence time and vice versa.

**Table 5. Reactor operation parameters during the experimental campaign.**

<table>
<thead>
<tr>
<th>CAMPAIGN</th>
<th>Variations in pressure</th>
<th>Variations in temperature</th>
<th>Variations in residence time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable</td>
<td>Unit</td>
<td>-P</td>
<td>0P</td>
</tr>
<tr>
<td>Pressure</td>
<td>bar(g)</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td>Black liquor mass flow rate</td>
<td>kg/h</td>
<td>487</td>
<td>645</td>
</tr>
<tr>
<td>Black liquor pre-heat temperature</td>
<td>°C</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>O2 mass flow rate</td>
<td>kg/h</td>
<td>151</td>
<td>196</td>
</tr>
<tr>
<td>λ</td>
<td>-</td>
<td>0.460</td>
<td>0.451</td>
</tr>
<tr>
<td>Normalized gas residence time</td>
<td>-</td>
<td>0.95</td>
<td>0.977</td>
</tr>
</tbody>
</table>

By varying the equivalence ratio λ from 0.40 to 0.45 the process temperature was changed from approximately 1020 °C to 1080 °C. During the measurements, system pressure and gas residence time were held close to constant. The gas residence time (τ) was decreased by a factor of approximately two by increasing the black liquor mass flow rate in two increments. The influence of primary spray flow rate on the gas composition was investigated at three different pressures and consequently three different reactor loads, see Table 6.

**Table 6. Quench operation parameters during the experimental campaign.**

<table>
<thead>
<tr>
<th>CAMPAIGN</th>
<th>Variation in primary spray flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variable</td>
<td>Unit</td>
</tr>
<tr>
<td>Pressure</td>
<td>bar(g)</td>
</tr>
<tr>
<td>Black liquor mass flow rate</td>
<td>kg/h</td>
</tr>
<tr>
<td>Black liquor pre-heat temperature</td>
<td>°C</td>
</tr>
<tr>
<td>O2 mass flow rate</td>
<td>kg/h</td>
</tr>
<tr>
<td>Primary Spray flow</td>
<td>l/h</td>
</tr>
<tr>
<td>λ</td>
<td>-</td>
</tr>
</tbody>
</table>
3 Numerical

There are a number of numerical tools that can be used to predict the behavior of a gasifier. Mass and energy balances can be used to estimate the mass and energy flows but does not provide any detailed information. Thermodynamic equilibrium codes, such as FactSage [53], become useful if the temperature is adequately high. The underlying assumption is that the system have stabilized at the lowest possible thermodynamic potential (such as the Gibbs free energy) at a given pressure and temperature. From this assumption the resulting phase and chemical equilibrium (of gas, solids and liquids) can be calculated using thermodynamic data (usually stored as polynomials). The benefit with thermodynamic equilibrium codes is that they can take many compounds into account and no reactions have to be specified since it is assumed that they are all at equilibrium. However, since the method does not consider the chemical reactions themselves (just the equilibrium state) the time scale is omitted in the equilibrium assumption. Since time is omitted (and consequently space) it is not possible to judge if the mixture will reach chemical equilibrium, it is simply assumed that it will. If the kinetics for the dominating reactions are fast i.e. that the temperature is adequately high this assumption has a small influence but at low temperature the calculations may be misleading.

Plug flow reactor calculations include the time dimension. In the calculations it is typically assumed that the considered species travel through a one dimensional pipe at a certain velocity, pressure and temperature. The evolution of the considered species can be calculated by discretizing the pipe in time and assuming that the species are perfectly mixed at each cross section. The calculations offer a great advantage over thermodynamic equilibrium calculations since the solution can be plotted in space. Hence, an estimate of the reactor size can be determined. However, the rate of each chemical reaction has to be specified and for a complex fuel this data is seldom known [54]. Furthermore, since it is assumed that the species are perfectly mixed at each cross section, effects of turbulence or recirculation are not taken into account. Both thermodynamic equilibrium (paper IV) and plug flow reactor calculations (paper V) were used to aid in the interpretation of the experimental results and in the development of the Computational Fluid Dynamics model described in the next section.
3.1 Computational fluid dynamics

In fluid dynamics, Computational Fluid Dynamics (CFD) was introduced in the 1960s [55]. Even though the method had been applied earlier [56], [57] computational power limited the usage and experimental and pure theoretical studies where dominating in comparison. The need for large computational power to solve the equations is associated with the small time and length scales in turbulent flows. To circumvent this, it is common to decompose the governing equation into a mean and a fluctuating contribution. However, the decomposition renders in a new problem.

In the Reynolds equations for mean–momentum\(^3\) (2) derived from the Navier-Stokes equations (1), the Reynolds stresses \(\langle u_i u_j \rangle\) are left as unknowns. In principle, equation (1) can be solved directly using known numerical techniques, rendering the Reynolds decomposition (equation 1 to 2) redundant. However, due to computational cost, the averaged Navier-Stokes will be used as a starting point for turbulence flow computations well into the foreseeable future [58]. In equation (1) \(\rho\) is density, \(p\) the modified pressure [58] and \(\nu\) is kinematic viscosity.

\[
\frac{DU}{Dt} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 U \quad (1), \quad \frac{D\langle U \rangle}{Dt} = \nu \nabla^2 \langle U \rangle - \frac{\partial \langle u_i u_j \rangle}{\partial x_i} - \frac{1}{\rho} \frac{\partial p}{\partial x_j} \quad (2)
\]

\[
\langle u_i u_j \rangle = \frac{2}{3} k \delta_{ij} - \nu_t \left( \frac{\partial \langle U \rangle}{\partial x_j} + \frac{\partial \langle U \rangle}{\partial x_i} \right) \quad (3)
\]

The Reynolds equations (2) are exact, i.e. there are no assumptions between the original Navier-Stokes formulation and the Reynolds equations, simply a decomposition where the velocity components \(U\) are expressed as a mean \(\langle \langle U \rangle \rangle\) plus a fluctuating contribution \(\langle u \rangle\). However, from the decomposition, the Reynolds stresses appear which have no corresponding equation. The problem is known as the closure problem, i.e. there are equations for the velocity components and for the pressure but not for the Reynolds stresses. One way around the closure problem is through the use of models relating the Reynolds stresses to functions of the mean velocity. The eddy viscosity hypothesis showed in equation (3) and used in the model described below does, if the turbulent viscosity field \(\nu_t\) is known, solve the closure problem. However, in contrast to the Reynolds decomposition the eddy viscosity hypothesis is an approximation that has some drawbacks but is widely used due to its simplicity and its ability to predict at least some practical flows with reasonable accuracy.

\(^3\) Incompressible, the pressure equation has intentionally been left out.
The physical interpretation of the turbulent or eddy viscosity is that it is a product between a characteristic turbulent “mixing” velocity and a turbulent “mixing” length. The turbulent viscosity field can be described using different approaches where the simplest is a constant turbulent viscosity. In the k-ε model used in this work the turbulent viscosity is defined as in (4).

\[ \nu_t = C_{\mu} \frac{k^2}{\varepsilon} \]  
(4)

Where \( C_{\mu} \) is one of five modeling constants used in the k-ε turbulence model. Still, given the definition of the turbulent viscosity additional equations are needed to relate the turbulent kinetic energy with the turbulent eddy dissipation. The transport equation for \( k \) can be derived exact, see equation (5).

\[ \frac{Dk}{Dt} = -\nabla \cdot T' + P - \varepsilon \]  
(5)

Where the flux \( T' \) is,

\[ T' = -\frac{1}{2} \left\langle u_i u_j \right\rangle + \left\langle u_i p' \right\rangle / \rho - 2\nu \left\langle u_i s_i \right\rangle \]  
(6)

In equation (6) \( p' \) is the fluctuating modified pressure and \( s \) the fluctuating rate of strain. In equation (5) \( P \) is half the trace of the production tensor.

\[ P = \frac{1}{2} P_x \quad \text{with} \quad P_x = -\left\langle u_i u_j \right\rangle \frac{\partial \left\langle U_j \right\rangle}{\partial x_i} - \left\langle u_i u_j \right\rangle \frac{\partial \left\langle U_j \right\rangle}{\partial x_i} \]  
(7)

In equation (5) the turbulent eddy dissipation (\( \varepsilon \)) and the flux (\( T' \)) are left as unknowns. Hence, even more equations are needed. The flux was modeled using a gradient diffusion assumption, see equation (8); notice the similarities with Ficks or Fouriers law.

\[ T' = -\frac{\nu'}{\sigma_k} \nabla k \]  
(8)

Where \( \sigma_k \) the turbulent Prandtl number for kinetic energy. Insertion of equation (8) into equation (5) yields equation (9), which is the model transport equation for the turbulent kinetic energy.

\[ \frac{Dk}{Dt} = \nabla \left( \frac{\nu'}{\sigma_k} \nabla k \right) + P - \varepsilon \]  
(9)
Still, the turbulent eddy dissipation is left as an unknown. In principle, the exact transport equation for \( \varepsilon \) can be derived. However, the standard model equation for \( \varepsilon \) used in this work is entirely empirical (see equation 10) [58].

\[
\frac{\partial \varepsilon}{\partial t} = \nabla \cdot \left( \frac{\nu}{\sigma_k} \nabla \varepsilon \right) + C_{\varepsilon} \frac{P_k}{k} - C_{\varepsilon 2} \frac{\varepsilon^3}{k} \tag{10}
\]

With \( \sigma_k \), \( C_{\varepsilon} \) and \( C_{\varepsilon 2} \) being model constants.

Close to walls the wall function approach described by Launder and Spalding [59] was used in the CFD model.

\[
u^+ = \frac{u^+}{u_c} = \frac{1}{k} \ln(y^+) + C \quad (11), \quad y^+ = \left( u^+ \Delta y \right) / \nu \quad (12)
\]

\[
u_c = \left( \frac{\tau_w}{\rho} \right)^{1/2} \quad (13), \quad \Delta y = \Delta n / 4 \quad (14)
\]

Where \( u^+ \) is the near wall velocity, \( u_c \) the friction velocity, \( \kappa \) the von Karman constant and \( \langle U \rangle \) is the velocity at distance \( \Delta y \) from the wall. \( C \) is a constant, \( \tau_w \) is the wall shear stress and \( \Delta n \) is the distance between the first and second grid point off the wall. As can be seen in equation (11), \( u^+ \) becomes zero when \( \langle U \rangle \) goes to zero. Particularly, at separation points this can become a problem. Instead, the near wall velocity (\( u^+ \)) can be expressed as in equation (15). Notice that the superscript * is used instead of + to separate the two descriptions. Finally, to ensure that all mesh points are outside the viscous sublayer a restriction was set on \( y^* \) (see equation 19), where the value 11.06 is the intersection between the logarithmic and the linear wall profile.

\[
u^* = C_{\nu}^{1/4} k^{1/2} \quad (15)
\]

With the friction velocity defined as equation (16).

\[
u_c = \frac{U_s}{\frac{1}{k} \ln(y^*) + C} \quad (16), \quad \tau_w = \rho u^+ u_c \quad (17)
\]

\[
u^* = \left( u^+ \Delta y \right) / \nu \quad (18), \quad y^* = \max(y^*, 11.06) \quad (19)
\]

The equations described above were used to calculate the motion of the single phase fluid, however in the black liquor gasifier there are also the black liquor particles present and these needs to be
The burner was modeled as a simplified spray burner with concentric annular inlets where oxygen and discrete black liquor droplets enter the gasifier at a prescribed range of angles and velocities. For a 2D geometry model the black liquor spray was represented by 1003 discrete particles having a fitted Rosin Rammler distribution of power 2 and characteristic size of 200 μm. The droplet size distribution and flow velocity are consistent with data from nozzle experiments measured by phase Doppler anemometry using a mixture of syrup and water as a black liquor analog [33], [48]. Particles impacting the reactor wall are assumed to bounce off without losing any momentum. On each particle there are forces acting, and vice versa the particle will exert a force on the surrounding fluid. In the calculations the forces acting on the particle are summarized in equation (20).

\[ m_p \frac{\partial U_p}{\partial t} = F_D + F_B + F_P \]  

(20)

where \( m_p \) is the mass of the particle, \( U_p \) the velocity of the particle and \( F_D, F_B \) and \( F_P \) is the drag, buoyancy and pressure gradient forces, respectively. The drag force was expressed as:

\[ F_D = \frac{1}{2} C_D \rho_f A_f \left( \frac{U_p}{\rho_f} \right)^2 (U_p - U_f) \cdot (U_p - U_f) \]  

(21)

where \( C_D \) is the drag coefficient and \( A_f \) is the particle cross sectional area. The buoyancy force was calculated according to equation (22) and the pressure gradient force according to equation (23).

\[ F_B = m_p \left( 1 - \frac{\rho_p}{\rho_f} \right) g \]  

(22)

\[ F_P = -\frac{m_p}{\rho_f} \nabla \rho \]  

(23)

The displacement of the particle and its instantaneous velocity can be calculated by solving equation (20) analytically and integrating over time. To include effects of turbulence on the discrete particles a turbulent dispersion model was introduced as suggested by Gosman and Ioannides [60]. The momentum source \( S \) (inserted on the right hand side of equation 1) can then be calculated as in equation (24). Notice that the buoyancy force \( F_B \) is left out since it has no contribution into the continuous phase.

\[ \frac{\partial S}{\partial t} = -(F_D + F_P) \]  

(24)

The equations above are not specific for combustion or gasification, but can be applied to all two-phase problems where the particle concentration can be considered low [61].
3.1.1 Material description and chemistry

In the CFD software the materials have to be described as specified species. Hence, the elemental or ultimate analysis needs to be transformed into the considered species. Based on the detailed elemental composition in Table 4, the ultimate analysis was simplified by lumping K together with Na and neglecting the Cl and N thus, forming a simplified material description of the modeled black liquor. The distribution of the elements was written as a row vector \((\text{ev})\) where \(\text{ev}(j)\) is the molar fraction of element \(j\) in the simplified ultimate analysis. The different species were then described by a matrix \(S\) defined as,

\[
S = \begin{bmatrix}
S_1 & \cdots & S_i & \cdots & S_n
\end{bmatrix}
\]

Where \(m\) is the number of considered species that should be present in the CFD-model and \(n\) is the number of elements in the element vector. The matrix elements \((S_{ij})\) describe how many moles of element \(j\) it takes to construct one mol of specie \(S_i\). From the species matrix \((S)\) and the element vector \((\text{ev})\) a system of linear equations (26) was formulated.

\[
S^T \cdot p = \text{ev}^T
\]

Where \(p(i)\) is the mol fraction for each respective specie. Since the number of model species was greater than the number of elements the system is underdetermined, that is, the number of unknowns \((p)\) was greater than the number of formulated equations \((\propto \text{ev})\). To resolve this, a constraint matrix \((C)\) and a constraint vector \((\text{cv})\) was defined and a similar system as in equation (26) was formulated. The matrix elements of \(C\) and the constraint vector \((\text{cv})\) were used to define ratios between the different species.

\[
C = \begin{bmatrix}
C_1 & \cdots & C_i & \cdots & C_m
\end{bmatrix}
\]

The linear system of equations described by (26) was solved using the least square method under the constraints described by (27).

\[
\begin{bmatrix}
A = S \cdot S^T & \Rightarrow A \cdot p = b,
\end{bmatrix}
\min_{p} \left[ A \cdot p - b \right]^T \text{subject to} \begin{bmatrix}
C \cdot p = c,
0 \leq p \leq 1
\end{bmatrix}
\]
The constraints that were used to obtain the model black liquor composition were as follows, all on mol basis:

- The distribution of combustible carbon between the char and the pyrolysis gas was 50%
- The ratio between CO and CO₂ was equal to unity in the pyrolysis gas
- 36% of the total sulphur is released during pyrolysis as H₂S
- The ratio between Na₂SO₄ and Na₂S was 8
- The concentration of NaOH in dry black liquor was specified to 0.50%
- All water is evaporated during drying

The composition obtained from this method is presented in Table 7. There is a small difference in the experimentally obtained heating value (Table 4, 12.57 MJ/kg) and the modeled heating value. To ensure consistency between the experimental results and the model, pyrolysis was modeled as a multiphase reaction with the heat of reaction equal to the difference in heating value divided by the volatile fraction in the dry particle. The constraints used to obtain the material description will be discussed further in section 4.4.

Table 7. Proximate analysis for black liquor used in the CFD calculations, higher heating value (HHV) is on dry basis.

<table>
<thead>
<tr>
<th>SIMPLIFIED ULTIMATE ANALYSIS</th>
<th>%wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>31.30</td>
</tr>
<tr>
<td>H</td>
<td>3.40</td>
</tr>
<tr>
<td>O</td>
<td>37.34</td>
</tr>
<tr>
<td>N</td>
<td>0.00</td>
</tr>
<tr>
<td>S</td>
<td>5.60</td>
</tr>
<tr>
<td>Na</td>
<td>22.36</td>
</tr>
<tr>
<td>K</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROXIMATE ANALYSIS Specie</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture %wt</td>
</tr>
<tr>
<td>H₂O(l)</td>
</tr>
<tr>
<td>H₂S(g)</td>
</tr>
<tr>
<td>CO₂(g)</td>
</tr>
<tr>
<td>Volatiles %wt</td>
</tr>
<tr>
<td>CO₂(g)</td>
</tr>
<tr>
<td>H₂(g)</td>
</tr>
<tr>
<td>CH₄(g)</td>
</tr>
<tr>
<td>Fixed carbon %wt</td>
</tr>
<tr>
<td>C(s)</td>
</tr>
<tr>
<td>Na₂SO₄(l)</td>
</tr>
<tr>
<td>Na₂S(l)</td>
</tr>
<tr>
<td>Na₂CO₃(l)</td>
</tr>
<tr>
<td>NaOH(l)</td>
</tr>
<tr>
<td>HHV MJ/kg</td>
</tr>
</tbody>
</table>
Considering the rotational symmetry, the reactor geometry was modeled as a 2D slice using periodic azimuthal boundary conditions. Regarding the wall boundary, estimates have shown that the heat loss in the plant through the reactor wall is approximately 90 kW or about 3 % of the total thermal throughput at full capacity. Since no detailed information was available regarding the heat loss distribution, heat losses in the CFD model were specified uniformly distributed along the wall. The radiative heat transfer was modeled using the discrete transfer radiation model by Lockwood and Shah [62] treating the wall as optically smooth with a radiative emissivity of 0.5. The absorption coefficient for the gas was calculated as the mass weight average of the participating species with coefficients for CO, CO2, H2O and CH4 taken from Barlow et al. [63].

The different black liquor conversion stages considered in the CFD model are shown in Figure 10. The initial droplet has the composition as showed in Table 7. The contained water evaporates and the particle devolatize giving a pre-defined fraction of species to the gas phase. When the temperature is adequately high the char starts to react with H2O, CO2 and Na2SO4 giving CO, CO2, H2 and Na2S as products. The mechanisms for these conversion stages have been described thoroughly by Marklund [33] and will not be repeated here.

For the gas phase, the simplified global reaction scheme by Jones and Lindstedt [64] was implemented as done by others [65] - [67] . To include turbulent mixing effects on reaction rates the Eddy Dissipation Model (EDM) [68] was used together with Finite Rate Chemistry (FRC). The EDM-FRC model calculates the turbulent mixing rate and kinetic reaction rate and uses the minimum (i.e. slowest) of the two. All reactions except the water gas shift reaction were modeled using the combined EDM-FRC concept. The water gas shift reaction was modeled using FRC thus ensuring that the reaction evolves towards equilibrium [69]. Regarding the sulfur chemistry in the gas phase, H2S (released during pyrolysis) was treated as inert.

In early stages of this work the results showed that all methane that was produced from the black liquor was completely consumed before the gas came to the outlet of the gasifier using the CFD model. The experiments on the other hand showed a methane concentration ranging from 0.5 % mol to about 2.5 % mol. The discrepancy in the predicted CH4 concentration led to large deviations in the main gas component concentrations (paper IV). To compare the simplified global reaction mechanism (which was believed to cause the discrepancy) with a more comprehensive mechanism plug flow reactor calculations were performed. The chemical kinetic program Cantera [70] was used with GRI-Mech 3.0 [71] as reference mechanism. The Jones and Lindstedt mechanism was compared to GRI-Mech with respect to methane conversion in a plug flow reactor at isothermal conditions with the following inlet molar gas composition: CH4: 10 %, CO2: 20 % CO: 20 %, H2O:
25 %, H₂: 25 %. The pressure was set to 27 bar and the temperatures to: 1273, 1400 and 1650 K. The result from the calculations is showed in Figure 11.

Figure 10. Reactions and species (mass fractions) considered in the CFD model. The diameters of the pie charts are proportional to the mass of a sphere and the thicknesses of the arrows are proportional to the mass flow.
Using the GRI mechanism, methane starts to reform at about 1400 K. After 5 s only 5 % have been converted into other species (mainly CO and H₂). At 1550 K (not showed in Figure 11), about 60 % have been reformed and at the highest temperature, 1650 K, almost all methane is reformed after 5 s. The Jones and Lindstedt mechanism shows a significantly higher reformation rate. At 1400 K, about 85 % of the methane has been reformed, which should be compared to 5 % for GRI-Mech. The PFR calculations confirmed that the reformation of methane is significantly over-predicted when using the Jones and Lindstedt mechanism in this temperature range. This comes as no surprise since the Jones and Lindstedt mechanism was developed for combustion. In a supplementary study (not presented here) the Jones and Lindstedt mechanism was compared to GRI-Mech in a counter flow oxygen methane jet flame and it performed fairly well given its simplicity. Additional PFR calculations were performed at different inlet gas composition with similar results (not presented here); the Jones and Lindstedt model showed significantly higher reformation rate of methane than GRI-Mech at gasification conditions in the medium temperature range.

**Figure 11.** Profiles of CH₄ molar fraction vs. residence time at different temperatures in an isothermal plug flow reactor at 27 bar. Solid line: GRI-Mech 3.0. Dashed line: Jones and Lindstedt. The inlet gas composition (mol) was CH₄: 10 %, CO₂: 20 %, CO: 20 %, H₂O: 25 %, H₂: 25 %. The reactor temperatures were: 1273, 1400, and 1650 K for each respective case. Temperature is constant along each curve.
range \((1150 < T < 1500 \, \text{K})\). Several attempts were made to optimize the coefficients in the Jones and Lindstedt model to fit both the hot flame region and the medium temperature post flame region but this was not successful. Agreement was obtained in one of the regions but not both using the same coefficients. To separate the flame and post flame region a limiter was introduced on the steam methane reforming reaction \((\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2)\), which forced the reaction rate to zero when the temperature was below 1400 K (see 4.4 Error estimation and uncertainties). The model was implemented in the commercial CFD software package Ansys CFX [40] where drying and pyrolysis were treated in a similar manner as char gasification and smelt formation through multiphase reactions implemented in FORTRAN subroutines. The numerical study consists of nine CFD calculations. The boundary conditions for all the calculations were taken as the measured values obtained from the DP-1 process monitoring system during the experimental campaign (see Table 5, page 21).
4 Results and discussion

The results obtained during the experimental and numerical campaigns will be discussed in this chapter. The chapter also contains a discussion regarding errors and uncertainties in the experiments and simulations. The gas composition is presented on mol basis as dry and nitrogen free with the lower heating value LHV in MJ/kg calculated from the measured gas composition.

4.1 Gas sampling equipment

Several measurement campaigns with the sampling probe were conducted in the gasifier. The left side in Figure 12 shows the concentration of CO₂, CO, H₂ and CH₄ close to the outlet of the reactor obtained with the high temperature gas sampling system and the sample obtained after the gas cooler during one of the experimental campaigns. Each data point corresponds to a certain combination of operational parameters.

During the experimental campaign 44 gas samples were withdrawn with the high temperature gas sampling system and several process parameters were varied systematically around the base operation condition, both in the reactor and the quench. The gas compositions from measurements with identical operating conditions are shown in the right column in Figure 12. The results show that the process yields nearly identical gas composition under identical operating conditions. The
measurements also showed that a change in operating conditions had a significant influence on the
gas composition. The average gas composition and the variation (± one standard deviation) during
base operation of the gasifier are summarized in Table 8. Notice that the standard deviation is about
1% of the measured value for CO₂, CO and H₂, for the minor components CH₄, H₂S and COS the
standard deviation is slightly higher.

### Table 8. Average dry gas composition ± one standard deviation during base operation condition of the gasifier

<table>
<thead>
<tr>
<th>Species</th>
<th>Probe measurements</th>
<th>After CCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ (% mol)</td>
<td>33.9±0.3</td>
<td>33.6±0.2</td>
</tr>
<tr>
<td>CO (% mol)</td>
<td>28.7±0.2</td>
<td>28.5±0.2</td>
</tr>
<tr>
<td>H₂ (% mol)</td>
<td>34.3±0.2</td>
<td>34.8±0.1</td>
</tr>
<tr>
<td>CH₄ (% mol)</td>
<td>1.36±0.07</td>
<td>1.44±0.07</td>
</tr>
<tr>
<td>H₂S (% mol)</td>
<td>1.65±0.04</td>
<td>1.71±0.02</td>
</tr>
<tr>
<td>COS (ppm mol)</td>
<td>468±22</td>
<td>122±5</td>
</tr>
</tbody>
</table>

In general, the trends in gas composition of the major gas components (CO₂, CO, H₂, CH₄, and
H₂S) at the exit from the hot zone of the reactor and after the gas cooler follow each other relatively
well. However, COS is significantly lower after the quench and gas cooler than in the reactor (see
section 4.3 Influence of quench operation on gas composition, page 44).

In the evaluation of the performance of the probe the concentration of CH₄ at the exit from the
reactor compared to the CH₄ concentration after the gas cooler is of special interest, since the
concentration of CH₄ can be regarded as relatively inert when the temperature of the gas is rapidly
reduced in the quench (see Figure 11, page 32). In all measurements (Figure 12), the CH₄
concentration after the gas cooler follows the concentration in the reactor and is almost identical.
This indicates that the fast quenching rate in the probe tip (~10 000 °C/s) was fast enough to freeze
all reactions of CH₄ and that the measured CH₄ concentration is representative of the CH₄
centration in the lower part of the hot reactor.

Figure 13 shows a photograph of the probe after the experiment. It is surprising that, for the
majority of cases, no significant amount of smelt could be found on the cooled surface; only a thin
layer of carbonized material (solid carbon) could be seen. After cleaning, no attack from corrosion
could be seen on the cooled surface of the probe. There are at least three possible explanations for
this phenomenon: i) It is likely that during the gasification process, solid carbon is formed on the
surface of the probe from the syngas. The properties of the solid carbon deposit prevent liquid
smelt droplets to stick to the probe surface and the droplet will therefore fall off the probe instead.
ii) The radiation from the cooled surface is sufficient to cool approaching smelt droplets below the
melting point and thereby make them non-sticky before they get in contact with the probe surface.
iii) Steam is condensed on the probe surface (due to the low surface temperature of the probe) and prevents smelt from sticking to the surface. As can be seen in Figure 13, the un-cooled probe tip suffered both from deposits and corrosion from the smelt.

![Gas sampling probe after it has been used in the gasifier; Carbon and smelt deposits on the cooled surface of the probe, notice that the anti-clogging shield has corroded away completely (upper). Close-up on the anti-clogging shield after approximately 12 hours of operation in the DP-1 gasifier (lower).](image)

4.2 Reactor measurement and computational results
The results presented in this section include the measured and calculated (using CFD) gas composition at variations in reactor pressure ($P$), equivalence ratio ($\lambda$) and residence time ($\tau$). All gas samples were withdrawn from the reactor using the high temperature gas sampling system. During the experimental campaign the gasifier was operated so that the monitored reactor process temperature was about 1050 °C (except when $\lambda$ was varied). However, at low reactor load, the wall heat losses will play a larger role in the heat balance for the reactor. Hence, to maintain constant temperature at decreased reactor load, the equivalence ratio was increased.
4.2.1 Variation of pressure
In the pressure variation experiments, the CO₂ content in the gas decreased with increased pressure (see Figure 14). The decrease is most likely an effect of the decrease in equivalence ratio in these experiments. Also, the increase of CO and H₂ can be related to the decrease in equivalence ratio. However, an alternative interpretation of the experimental results from pressure changes is that more CO₂ absorb into the smelt forming Na₂CO₃, H₂S and COS according to reactions R20 and R21 at elevated pressures (Table 5 reactions R20 and R21, shift towards the right at increased pressure). Furthermore, the H₂S content increase as pressure increase, which could support this interpretation. Apart from this, no significant system pressure dependency can be detected. The weak pressure dependency is expected since; the main reaction determining the bulk gas composition appears to be the water gas shift reaction (reaction R9) which has no pressure dependency according to the Le Chatelier's principle. On the other hand, the steam methane reforming reaction has a pressure dependency where an increased pressure will shift the equilibrium towards the side with fewer moles (reaction R10 towards left). However, it is possible that; given the relatively slow kinetics (see Figure 11, page 32) for the reaction explains why a pressure dependency is not detected. The CFD-predictions for the main gas components are within a relative error of approximately 5 %. However, the trends are not well predicted for CO and CO₂. The experimentally obtained values show a clear decrease in CO₂ and increase in CO when pressure is increased and this is not captured by the model. The trend in CH₄ also suggests that the middle pressure point (0P 20 bar) is the operating condition that deviates from the trend. The relative error in CH₄ is similar for the low and high pressure case but is about two times as large for the medium pressure case. However, the trend in H₂ concentration is predicted, i.e. an increase in concentration with an increase of pressure. H₂S show the second largest relative error at about 25 %. H₂S is treated as an inert in the model and hence will not be influenced by the operating conditions. The calculated outlet concentration of about 1.7 % (see Table 9) will instead be dictated by the initial release of H₂S (see Table 7, page 29). The predicted char carbon conversion and outlet temperature are the highest at the medium pressure point by 98.8 % and about 1245 K respectively (Figure 15).

4.2.2 Variation of equivalence ratio
Even though some differences can be seen for all gas components when the equivalence ratio is varied, the most significant difference is found for CH₄. CH₄ decrease from 2.72 % to 0.76 % when the equivalence ratio was changed from 0.39 to 0.45. The monitored reactor temperature changed from approximately 1020 °C to 1080 °C during the experiments when these variations were made. For the bulk gas components (CO, CO₂ and H₂), the increase of CO with increasing λ is the most
dominant effect. It is also possible to distinguish a reduction of H$_2$ and an increase of CO$_2$ when $\lambda$ is increased.

As in the pressure variation experiments, the heating value decreases significantly with increased equivalence ratio. The heating value of the gas decreased approximately 10 % when $\lambda$ was increased. However, if CH$_4$ is considered inert, the heating value of the gas is only reduced by approximately 3 %. Hence, if the gas is intended as feedstock to a fuel synthesis plant a significant amount of the CH$_4$ can be converted to active components (CO, H$_2$) in the gasifier without reducing the heating value of the bulk gas considerably. The CFD-results for this case are encouraging. The increase in CO with increased equivalence ratio is captured as well as the decrease in H$_2$. In the experiments an increase in CO$_2$ was observed, which is not captured by the model. However, the increase in CO$_2$ observed in the experiments is relatively small, about 0.7 percentage points, which corresponds to approximately two standard deviations. The largest relative error can be found for methane in the low temperature case but encouragingly the error is significantly smaller at the higher equivalence ratios. The trend in CH$_4$ is also predicted correctly. Figure 15 shows that an increase in equivalence ratio leads to an increase in char carbon conversion and the difference is about 10 percentage points between the high and low equivalence ratio cases. The mean, outlet and probe position temperatures all increase when the equivalence ratio is increased.
4.2.3 Variation of residence time

The residence time experiments were conducted at constant pressure, that is, an increase in residence time was achieved by decreasing the black liquor mass flow rate and vice versa. Since the thermal power is changed when the black liquor mass flow rate is changed, the influence of the wall heat losses will be greater at long residence time i.e. low black liquor mass flow rate than at higher black liquor mass flow rate.

The short and medium residence times have almost equal equivalence ratios and the methane concentration is almost constant for these two residence times. The model predicts this trend fairly well. However, at the longest residence time the trend is lost even though the absolute value is closer to correct. The predicted methane has the largest relative error in the short and medium residence time cases (around 45 %). This error is also reflected in the prediction of CO with a relative error of 9 % at the shortest residence time. This is the largest error for the main components in the entire set of simulations. Because of the discrepancies in CH₄ predictions, the trend predictions for the main gas components are not as clear. The trend in CO₂ is somewhat captured with fairly constant values at the short and medium residence time and an increase at the longer residence time. For CO and H₂ there is no clear trend from the model. The char carbon conversion decreases at the longer residence time compared to the shortest and so do the temperatures.
4.2.4 Variation of operating conditions summary

The results from the process conditions variation are summarized in Table 9. As can be seen in Table 9 the predictions of the main gas components show an overall good agreement; absolute values are within 2.5 %, and relative errors for major gas components within 9.0 %. The lower heating value is predicted very well for all the cases and the largest relative error can be found for the low temperature case (-λ) at -4.6 %.

Table 9. Experimental and numerical results (CFD), units are % mol and MJ/kg. Boundary conditions are according to Table 5.

<table>
<thead>
<tr>
<th>CAMPAIGN</th>
<th>Case</th>
<th>CO2 STD ±0.3 Exp.</th>
<th>Num. Rel. error</th>
<th>CO STD ±0.2 Exp.</th>
<th>Num. Rel. error</th>
<th>H2 STD ±0.2 Exp.</th>
<th>Num. Rel. error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variations in pressure</td>
<td>-P</td>
<td>37.1 36.1</td>
<td>-2.7%</td>
<td>27.4 28.6</td>
<td>4.2%</td>
<td>33.0 32.7</td>
<td>-0.8%</td>
</tr>
<tr>
<td></td>
<td>0P</td>
<td>35.5 34.5</td>
<td>-2.8%</td>
<td>28.4 29.3</td>
<td>3.1%</td>
<td>33.3 33.7</td>
<td>1.3%</td>
</tr>
<tr>
<td></td>
<td>+P</td>
<td>34.0 35.1</td>
<td>3.3%</td>
<td>28.7 27.2</td>
<td>-5.3%</td>
<td>34.2 34.8</td>
<td>1.8%</td>
</tr>
<tr>
<td>Variations in temperature</td>
<td>-λ</td>
<td>34.1 34.7</td>
<td>1.8%</td>
<td>25.6 26.2</td>
<td>2.4%</td>
<td>35.6 35.5</td>
<td>-0.2%</td>
</tr>
<tr>
<td></td>
<td>+λ</td>
<td>34.8 34.5</td>
<td>-1.0%</td>
<td>28.5 27.2</td>
<td>-4.7%</td>
<td>34.1 34.8</td>
<td>2.2%</td>
</tr>
<tr>
<td>Variations in residence time</td>
<td>-τ</td>
<td>35.0 33.4</td>
<td>-4.5%</td>
<td>27.4 29.9</td>
<td>9.0%</td>
<td>34.6 34.2</td>
<td>-1.1%</td>
</tr>
<tr>
<td></td>
<td>+τ</td>
<td>37.1 37.3</td>
<td>0.4%</td>
<td>27.5 26.0</td>
<td>-5.4%</td>
<td>32.6 33.6</td>
<td>3.0%</td>
</tr>
</tbody>
</table>

When the process conditions are varied, the largest error for the main gas components can be found in the short residence time experiment. The absolute error for CO is 2.5 %, which corresponds to 9 % on a relative basis. For the same case, the methane prediction also shows the largest relative error of about 45 %.
4.2.5 Conversion of carbon containing species

Figure 16 shows the predicted methane concentrations and char carbon conversions against the predicted outlet temperatures and equivalence ratios. The char carbon and CH₄ conversions both increase with increased temperature. However, the trend is not as clear when the same results are plotted against the equivalence ratio (right parts in Figure 16). The discrepancies that can be seen for the CH₄ prediction (particularly for the cases 0P, -λ, +τ and 0τ) may be associated with the wall heat loss. In the simulations the heat loss was assumed constant at 90 kW (uniformly distributed at the wall) for all the cases. A constant wall temperature would yield a constant ΔT across the refractory and hence a constant heat flux but this may not be the case since the temperature measurement may be wrong or the wall heat loss not uniform. The temperature in DP-1 is measured with wall mounted thermocouples, which may not measure a representative temperature but rather a mixed result of radiation from the flame, the walls, the gas and convection from the gas. The experimental results imply that the heat loss is smaller at reduced thermal power/black liquor flow rate. If the heat loss is smaller this would result in higher reactor temperature and hence reduced methane concentration in the outlet gas. The discrepancies may also be explained by differences between the actual and the prescribed spray characteristics.

During the experimental campaign the char carbon conversion in the DP-1 black liquor gasifier was very close to complete since no char carbon was found in the green liquor or the green liquor dregs. However, the model is not able to predict full conversion for any of the simulated cases. The char carbon conversion for the base case (0λ, +P) predicted by the model is about 96 %, which results in the same order of relative error as for the main gas components. The predicted char carbon conversion for the low temperature case (-λ) is about 88 %, which is significantly lower than the estimated one 99.95 %, Furusjö E. (personal communication February 4, 2011). This may be a result of uncertain char conversion rates but does not hinder that the model is used for optimization or scale-up. The low temperature operating point (-λ) is not favorable in the DP-1 gasifier (may cause fouling in downstream equipment). Hence, even if the predicted char carbon conversion is lower than in the DP-1 gasifier the predictions still provide useful information for finding favorable operating conditions for a larger gasifier or for optimization.

Some of the samples taken from the DP-1 gasification reactor were analyzed with respect to larger hydrocarbons than CH₄. The analysis showed that benzene was the hydrocarbon with highest concentration next to CH₄ with concentrations ranging from about 80 - 200 ppm depending on operating conditions. All other hydrocarbons had a concentration significantly lower than that. However, there are still other hydrocarbons present in the reactor. After the measuring campaign the gas sampling probe was rinsed with a solvent (dichloromethane) and the resulting solution was
analyzed with a GC-MS. Detectable amounts of several hydrocarbons (phenanthrene, dibenzothiophene, fluorine and others) were found. Unfortunately, the corresponding concentration in the reactor could not be quantified.

Figure 16. Upper: Simulated CH₄ outlet concentration as function of simulated outlet temperature (left) and CH₄ as function of equivalence ratio (right) obtained from the simulations and from experiments (filled circles). Lower: Char carbon conversion obtained from the simulation as function of outlet temperature (left) and equivalence ratio (right).
The influence of primary spray flow rate on the gas composition was investigated at three system pressures: 15, 20, and 27 bar. The absolute values of the gas composition in the reactor and the quench can be found in paper III. Here the focus will be on the relative change in composition (Figure 17 and Figure 18) when the gas passes through the quench i.e. if the concentration of a specie increase as it passes through the quench the relative change will be positive and vice versa.

At all pressures (15, 20 and 27 bar), the concentration of COS was significantly lower after the quench than in the reactor. For the base operating condition about 25 % of the COS originating from the reactor remains in the cool raw gas exiting the CCC. Even though the COS concentration increased with increased primary spray flow it was still significantly lower after the CCC than in the reactor. Considering CO₂, the concentration is lower after the quench compared to the reactor for all pressures and all primary spray flow rates but in contrast to COS concentration the CO₂ concentration decreases with increased primary spray flow rate.

For CO and H₂ the results are slightly different. CO increase with increased primary spray flow rate at all pressures but has a higher concentration after the CCC than in the reactor at 15 bar (Figure 17). At 20 and 27 bar, the concentration after the CCC is lower than in the reactor apart for the highest primary spray flow rate (Figure 18). H₂ concentration is higher after the CCC than in the reactor at 15 bar and appear to increase with increased primary spray flow. At 20 and 27 bar the H₂ concentration is still higher after the CCC than in the reactor but here the concentration appears to decrease with decreased primary spray flow rate. Due to the relatively large variations in the reactor concentration of H₂S between the experiments, it is hard to determine the true influence of the
primary spray flow rate on the change in H₂S concentration. However, the results suggest that the concentration of H₂S after the CCC is higher than the concentration in the reactor. This indicates that sulphur was released to the gas phase from the smelt droplets or fume particles suspended in the gas and/or from the green liquor pool. One possible explanation based on reaction Q4, is that H₂S can be released to the gas phase when Na₂S (as smelt droplets or fume particles) reacts with H₂O and CO₂ in the gas producing Na₂CO₃ and H₂S in the primary quench zone. Furthermore, depending on the pH (amount of absorbed CO₂) in the green liquor, the acid H₂S can either be absorbed or released to the gas phase (Q7).

![Graph showing influence of primary spray flow rate on gas composition at 20 bar (left) and 27 bar (right) pressure.](image)

The results presented above show that the major components in the raw gas are affected as they flow through the quench. As an example, the H₂/CO mol ratio was in some cases found to be significantly higher after the CCC than in the reactor. The cause of this is believed to be the interaction between water from the primary spray and the hot raw gas from the reactor. The results also indicate that this effect is enhanced by increased system pressure. Since the black liquor and oxygen mass flow rate (load) was scaled with pressure during the experiment (see Table 6 on page 21), it appears that the ratio between the primary spray flow rate and the reactor load has a significant influence on the H₂/CO mol ratio in the cooled raw gas. In order to verify this hypothesis, the H₂/CO mol ratio in the reactor and after the CCC was plotted against the load (see Figure 19).
For high primary spray flow rate/load ratios the \( \text{H}_2/\text{CO} \) mol ratio in the reactor and after the CCC was almost the same (approximately 1.2). However, when the primary spray flow rate/load ratio was reduced below approximately 0.6, the \( \text{H}_2/\text{CO} \) mol ratio after the CCC increased significantly compared to the \( \text{H}_2/\text{CO} \) molar ratio in the reactor. For a primary spray flow rate/load ratio of 0.2 the \( \text{H}_2/\text{CO} \) molar ratio after the CCC is about 1.4 compared to 1.15 in the reactor. The apparent change of the major gas components as the gas flows through the quench are most likely explained by the water gas shift reaction (Q1). The partial pressure of water vapor in the gas is increased in the quench due to extensive evaporation of water from the primary spray, which reduces the gas temperature. Both the increased partial pressure of water vapor and the reduced gas temperature shift the equilibrium gas concentration to more \( \text{H}_2 \) and \( \text{CO}_2 \) produced from \( \text{CO} \) and \( \text{H}_2\text{O} \). For high primary spray flow rate/load ratios (> 0.6) the cooling rate of the gas (and associated temperature drop) is probably high enough to prevent the water gas shift reaction to alter the composition. The result is a gas composition after the quench that is almost identical to the gas close to the exit of the hot reactor.

![Figure 19. \( \text{H}_2/\text{CO} \) ratio in the reactor and after the gas cooler as a function of the primary spray mass flow rate over load (black liquor and \( \text{O}_2 \) mass flow rate). Complementing values are taken from paper III.](image)

However, for low primary spray flow rate/load ratios (< 0.6) the temperature after the primary spray region is probably still sufficient to permit a shift in the gas composition towards more \( \text{H}_2 \) and \( \text{CO}_2 \) and lower amounts of \( \text{CO} \) (Figure 20). The observed reduction in \( \text{CO}_2 \) concentration when the gas flows through the quench for very large primary spray flow rate/load ratios indicate that some \( \text{CO}_2 \) was absorbed by the green liquor or by smelt droplets in the quench. The temperature in the quench is reduced by the cooling water introduced via the primary spray and if enough water is introduced the syngas will be saturated with water vapor. Water droplets from the primary spray
then survive (do not evaporate) in the saturated gas above the green liquor surface, which result in collisions with smelt droplets or with inorganic fume particles, forming small alkaline green liquor droplets (Q5-Q7). Acid CO$_2$ in the gas may thereafter be absorbed in these green liquor droplets (Q8), which would lower the pH in the droplets. This would in turn reduce the quality of the final green liquor (Q9-Q14). Thus, for operating conditions resulting in a saturated gas, a further increase in primary spray flow rate/load ratio will increase the number of surviving water droplets in the gas results in an unwanted CO$_2$ absorption in the final green liquor. The water gas shift reaction (Q1) and the absorption of CO$_2$ in the green liquor are likely to be the main explanations for the influences of the different operating parameters on the gas composition that was observed in the experiments.

Figure 20. Influence from primary spray flow rate to load ratio on the absolute difference (mol %) in major gas composition when the gas flows from the reactor through the quench. Complementing values are taken from paper III.
4.4 Error estimation and uncertainties

In this section the errors and uncertainties regarding the CFD model and the experiments will be discussed. The focus regarding the CFD model will be on validation and verification. Verification in this context means to make a: “substantiation that a computerized model represents a conceptual model within specified limits of accuracy” and validation to make a: “substantiation that a computerized model within its domain of applicability possesses a satisfactory range of accuracy consistent with the intended application of the model” [72]. The methodology is schematically showed in Figure 21. The conceptual model is the general understanding of the underlying mechanisms, and the computerized model is the numerical interpretation of the conceptual model.

![Figure 21. The CFD paradigm, phases in modeling [73]](image)

Validation is often confused with comparison. For example, with the black liquor gasification model described in this thesis one could claim that the “model have been validated against experimental result and show good agreement”. This is not the case, the calculated gas composition show good agreement when compared to experimental results but a formal validation would include measurement of turbulent quantities, velocity and temperature field, spatially resolved gas measurements, particle wall interaction etc. However, the lack of this data does not render the model unfeasible. The results from the model are still in good agreement with the experimental results regarding gas composition and char carbon conversion and give plausible predictions of the velocity and temperature field. Future experiments can reveal if the predictions are correct.
There are uncertainties related to the CFD model that need to be verified. The numerical related uncertainties such as discretization error, round-off errors and iteration error were addressed in the following way. The discretization error was estimated using Richardson extrapolation [74] to 0.04 % based on the volume average temperature and 2 % based on the volume average velocity with a corresponding Grid Convergence Index (GCI) of 0.01 % and 1.1 % respectively, both methods (Richardson extrapolation and GCI) have been discussed extensively in the literature [75] and are recognized as feasible quality-control measures for numerical computations. Three different meshes were used in the study with 20400, 77740 and 296032 hexahedral elements, respectively. Round off errors were not estimated but were minimized by using 64-bit storage during the calculation i.e. double precision. The iterative error was reduced by letting the normalized residuals be reduced by at least three orders of magnitude and by having a global conservation target less than 0.1 %. 

The k-ε turbulence model, which has known deficiencies, was used in the CFD-calculations. For example, the spreading rate of round jets are known to be over-predicted [58] using this model. This could result in that the calculated flame is shorter than the actual. It is possible that a more advanced turbulence model (such as a Reynolds stress model) would yield a different result but it would also introduce numerical difficulties and in the end, perhaps not give more accurate results than the present model [76].

The conversion of methane in a plug flow reactor with gas composition representative of rawgas has been experimentally investigated by Valin et al. [77]. In their study they obtained about 18 % conversion of CH₄ at a residence time of 2.1 s and a temperature of 1400 K. In the CFD-simulations, 1400 K was set as the extinction temperature for the steam methane reforming reaction in order to get reasonable predictions. This is slightly higher than the temperature at which negligible conversion was obtained by Valin et al. It is possible that an even higher extinction temperature would result in improved predictions of the CH₄ concentrations. However, 1400 K was considered a reasonable value based on the results from the PFR calculations and the experimental results obtained by Valin et al [77].

In an early stage of the present work a more comprehensive gas phase reaction mechanism [78] was considered for the CFD model calculations. However, this approach turned out to be computationally too expensive and difficult to control regarding numerical stability. Hence, the current extinction temperature approach was chosen even if there are some uncertainties around the reaction mechanisms regarding the conversion of methane. Furthermore, there are catalytic effects present and uncertainties in the pyrolysis gas composition, which in the real case involves several
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hydrocarbon species [41] that will affect the outlet gas composition. The composition of the pyrolysis gas and the char yield has been examined by Sricharoenchaikul et al. [41] - [43] in a laminar entrained flow reactor. At 1000 °C, about 65 % [43] of the dry black liquor could be found as char residue; in the current model this value is about 70 % which is of similar order (see Figure 10, page 31 droplet after drying). Sricharoenchaikul et al. further showed that the CO/CO2 ratio in the pyrolysis gas has a temperature and residence time dependency [41]. Since CO and CO2 may be formed from secondary reaction in the gas phase it is difficult to define an accurate single value for the CO/CO2 pyrolysis gas ratio. The H2S released during pyrolysis was constant in all calculations. This will influence the results, not just for the H2S concentration. Marklund [79] showed that an increase of H2S in the gas will effectively lead to a reduced reactor temperature and thus char carbon conversion since more of the char is converted through the gasification reactions than by the sulphate reduction reaction. Thus, even if a more comprehensive reaction scheme had been applied in the present case there is no guarantee that the outlet gas composition would have been predicted more accurately since there are uncertainties in the pyrolysis gas composition. These uncertainties are also reflected in the proximate analysis model (described in section 3.1) even if the assumptions are based on available experimental data.

The CFD-paradigm showed in Figure 21 does not illustrate that the numerical results are not compared to reality, but the observed reality. Hence, the CFD paradigm needs to complimented with how the reality is perceived i.e. which methods are used, how large are the experimental errors and can the results be replicated (see Figure 22).

![Figure 22. Phases in the experiments and computer modeling performed in this work](image-url)
In this work a gas sampling probe was used to gather data from the gasification reactor. The performance of the probe relies on fast quenching of the gas thus ensuring that the extracted gas is representative of the gas inside the gasification reactor. Based on the temperature measurements during sampling it was estimated that the cooling rate in the probe was about 10,000 °C/s. Plug flow reactor calculations can be used to show that the main gas components are frozen at about 900 °C using GRI-Mech 3.0 as mechanism. Assuming that the gas temperature is about 1100 °C inside the gasification reactor (which is higher than both calculated and the measured process temperature) this would render in a “time to react” (between 900-1100 °C) of about 0.02 s that could change the gas composition for the main components about 0.25 % on a relative basis or approximately four times less than the standard deviation showed in Table 8. Considering that uncertainties originating from small variations in process parameters (flow measurement etc.), liquor composition (variations in sulphur and solids content etc.) and analytical uncertainties (when analyzing the gas samples) are included in the standard deviation the current sample method appears reliable and has proven repeatability.
5 Conclusions

There have been three conjunctive activities performed within this thesis; development of experimental equipment, retrieval and interpretation of experimental data and improvement of a numerical model. The main goals were to i) increase the understanding about the dominating mechanisms in black liquor gasification and ii) develop an engineering tool that can be used to design and optimize pressurized, entrained flow, black liquor gasifiers.

In the development of the gas sampling probe it was discovered that a water-jacketed sampling probe will survive the conditions inside the reactor for a long time if sufficient cooling is maintained. It was also discovered that smelt droplets will not adhere to the cooled surface of the probe. On uncooled surfaces such as the probe tip deposits will form and corrosion will be severe. Careful design of the probe tip is crucial in order to prevent plugging during gas sampling. The probe was operational after 44 gas samples had been withdrawn and the obtained results showed good repeatability.

Even though the actual conversion mechanisms in the reactor are very complex it appears that they can be described with relatively simple sub models. The main gas components are dictated by the water gas shift reaction. This hypothesis was first put forward in paper II and was later confirmed in paper IV and V. The gas composition is not in global thermodynamic equilibrium at the outlet of the gasifier. However, the main gas components are close to partial equilibrium whilst CH₄ and H₂S are not (see paper IV). Very little of the available CH₄ is reformed outside the flame region and the primary consumption occurs in the flame through oxidation and reformation. Increased system pressure promotes H₂S in the gas, as well as a decreased equivalence ratio.

In the quench the primary spray flow rate/load (mass flow of black liquor and oxygen) ratio has a critical value of about 0.6 below which the gas concentration of CO₂, CO, and H₂ change significantly. The H₂/CO ratio can be changed from about 1.15 to 1.4 by changing the primary spray flow rate/load ratio. The explanation for this is that, for high primary spray flow rate/load ratios the temperature is reduced adequately fast to prevent any significant influence from the water gas shift reaction. Therefore the gas concentration after the quench is nearly the same as in the hot reactor. For low primary spray flow rate/load ratios, the sustained temperature causes more influence from the water gas shift reaction thus shifting the gas composition towards more H₂ and CO₂ and less CO. The concentration of H₂S after the CCC increased while the concentration of COS was reduced compared to the reactor. The increase in H₂S after the quench cannot be explained solely by hydrolysis of COS. A likely mechanism is release of H₂S from smelt droplets or fume particles in the primary quench zone and/or from the green liquor pool.
6 Future work

The probe was installed in the lower part of the gasification reactor. Hence, the gas composition obtained using the method can be regarded as a volume average in the vicinity of the outlet. It is of great interest to characterize the gas composition closer to the burner in the reactor. If this is done simultaneously as a sample is taken from the lower part of the reactor it may be possible to estimate the kinetics for the main gas components in the reactor. Even though the CFD model contains the water gas shift reaction the used available kinetics are taken from idealized conditions. If spatial data was available an apparent reaction rate could be determined and be compared to the existing. Furthermore, if the probe was complemented with possibilities to measure condensables (e.g. steam and tars), temperature and particulates this could provide insights both to the applicability of the CFD model and increase the understanding of the reactor characteristics for different burner installations and operational conditions.

Optical access to the reactor could provide information regarding spray and flow field characteristics, particle-wall interaction and particle residence time measurements. If more advanced optical equipment was used this could also provide information regarding flame characteristics, concentration profiles and black liquor particle swelling. In the quench similar measurements could be performed. Water spray smelt interaction and gas quench pool interaction could provide valuable data for both understanding the mechanisms and for modeling.

Idealized experiments that focus on the validity of the assumptions in the CFD-material description, particular the mechanisms and distribution of Na$_2$SO$_4$-Na$_2$S-H$_2$S, and time resolved measurement of the pyrolysis gas would increase understanding as well as provide modeling input. Regarding the used sub-models, more advanced chemistry is still of interest even if this has showed to be problematic. Furthermore, the gas residence time in the reactor will be determined by the level of entrainment (close to the burner) and the dissipation of the jet, if this was first visually characterized it could be compared to calculations using different turbulence models.

It seems that many of the discrepancies in the CFD results can be explained by improper wall boundary conditions. In future work it may be more appropriate to include the refractory in the simulations (and use a fixed temperature boundary condition at the outside of the refractory) to see how it will influence the results, particularly the heat distribution and heat loss.
7 References


8 Appendix

**Paper I**

**Paper II**

**Paper III**

**Paper IV**

**Paper V**
Carlsson P., Lisa K., Gebart R., Predicting the outlet gas composition from a black liquor gasifier using CFD – Comparison with experiments. Submitted to Energy & Fuels
Design and methodology of a high temperature gas sampling system for pressurized black liquor gasification

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Abstract
This paper describes the system design and methodology for high temperature gas sampling during pressurized black liquor gasification. The motivation for developing a system that can withstand the harsh conditions in the reactor part of the gasifier (30 bar, 1000°C, reducing conditions and corrosive environment) comes from an ambition to better understand the various stages in the conversion of the fuel (black liquor) and provide spatially resolved data of the gas composition inside the gasification reactor. Important components in the high temperature sampling system which are all described in detail in the paper, are the syngas sampling line, nitrogen purging system, water cooling line and an aerodynamic quench probe with an anti-clogging shield. Several measurement campaigns have been conducted in the gasifier where the concentration of CO2, CO, H2, CH4, H2S, and COS close to the outlet of the hot reactor have been measured with the high temperature gas sampling system. The results showed that the repeatability of the measured gas composition was excellent and that significant effects on the gas composition from different operating parameters of the gasifier could be found.

1. Introduction
Black liquor, a by-product of the chemical Kraft pulping process, is an important liquid fuel in the pulp and paper industry [1]. It consists roughly of 30% water, 30% inorganic cooking chemicals (valuable for the pulp mill) and 40% lignin and other organic substances separated from the wood during chemical pulping in a digester. A novel technology, for the recovery of black liquor is Pressurized Entrained-flow High Temperature Black Liquor Gasification (PEHT-BLG) [2]. In combination with either a gas turbine or a catalytic fuel synthesis process a significant amount of green electricity or second generation motor fuels can be produced with this technology. To obtain a proof of the concept, a Development Plant (DP1) with a capacity of 20 ton dry solid of black liquor/24 h (~3 MWth) was commissioned in 2005 by the technology owner Chemrec AB. The gasifier is located next to the Smurfit Kappa Kraft-liner pulp and paper mill in Piteå, Sweden. The DP1 is fully instrumented and is operated continuously by a 5-shift operating team to provide proof that the technique is sufficiently robust for industrial use and to provide valuable data for scale-up of the process.

The main components of the PEHT-BLG process are shown schematically in Fig. 1. A refractory lined entrained-flow gasification reactor, with a gas assisted burner centrally placed on top producing small black liquor droplets is the main process vessel. Pressurized (30 bar) high temperature (~1000°C) entrained-flow gasification takes place there, mainly through reactions with oxygen, steam and carbon dioxide producing a syngas and a liquid smelt mainly consisting of Na2CO3 and Na2S. Beneath the reactor is a quench cooler where the syngas and smelt are quenched and separated. The majority of the smelt particles are dissolved in the quench water forming green liquor but the smallest particles will remain suspended in the gas. The syngas then passes through a Counter Current Condenser (CCC) that cools the syngas. The resulting condensation of water vapor and tar species will take place on particles in the gas that as a result will become too heavy that suspension becomes impossible. Hence, the CCC acts as an efficient particle scrubber. The heat recovered from the gas is used to generate low/medium pressure steam that can be used in the pulp and paper process, from which the black liquor is originated.

In order to increase the understanding of the various stages of black liquor conversion in the gasification process and to provide spatially resolved data of the gas composition inside the hot reactor, an in situ gas sampling system that withdraw gas from the hot reactor part (see Fig. 1) was designed. The data (gas composition inside the reactor) will later be used as validation for mathematical...
models of the process (CFD and thermo-chemical equilibrium) and as input for process optimization.

The design of the sampling system and the probe itself is a challenging task due to the high temperature ($\sim$1100°C), high pressure (30 bar), high smelt loading and reducing conditions ($\sim$ 0.4) inside the gasifier. Furthermore, the environment inside the gasifier is very corrosive and plugging of the sampling probe caused by the high particle loading inside the reactor is problematic. Furthermore, since we working with high pressure and gasification gas, which are both poisonous and explosive in contact with oxygen, a small leakage of gas from the sampling system may cause catastrophic effects. Therefore, the design of the measurement system must fulfill several safety aspects before it can be installed and operated. To the authors knowledge, no measurement system that withdraws syngas from the hot reactor of an industrial pressurized slagging gasifier (black liquor, biomass or coal) has earlier been described in the literature. The aim of the current paper is therefore to describe a safe and well functional gas sampling system for such an environment.

2. High temperature gas sampling system

In Fig. 2, a sketch of the high temperature gas sampling system can be seen. As the gas sampling system handles inflammable and explosive gases it was designed in compliance with ATEX [3,4], IEC
61508, and IEC 61511 directives. The sampling system consists of; the gas sampling line, the water cooling line and the gas sampling probe. These are all described in more detail in the following sections.

In the description of each component, the superscript G refers to a component in the gas sampling line and superscript W refers to a component in the water cooling line. The abbreviation TC stands for thermocouple, FI stands for flow indicator, PG stands for pressure gauge, AV stands for a valve that is automatically controlled by the control system of the gasifier and finally, MV stands for a valve that is manually controlled by the operator of the sampling system.

2.1. Gas sampling line

The gas sampling line consists of the following components from the probe tip and downstream: An orifice with a diameter of 1.5 mm mounted at the probe tip in order to restrict the maximum possible syngas flow out from the reactor; A thermocouple (TC-1G) measuring the gas temperature close to the probe tip; Another thermocouple (TC-2G) measuring the gas temperature close to the outlet of the probe; Two automatically controlled ball valves (AV-1G and AV-2G) controlling the syngas or nitrogen flow out or into the reactor.

If the temperature after the probe (TC-2G) exceeds 150 °C during a measurement the two ball valves (AV-1G and AV-2G) are automatically closed. A visually inspected pressure gauge (PG-1G), measures the pressure in the sampling line. Downstream the pressure gauge the gas sampling line is divided into two separate systems, the nitrogen purge system and the syngas sampling system.

2.1.1. Nitrogen purge system

The pressure in the nitrogen purge system is kept above the reactor pressure and is controlled by two ball valves. The first ball valve (MV-1G) is operated manually and the second ball valve, (AV-1G), is automatically controlled. A flow indicator (FI-1G) measures the mass flow rate of nitrogen to the probe. To prevent fouling at the probe tip, a nitrogen purge flow of 0.1 kg/h is maintained at the maximum possible syngas flow out from the reactor.

2.1.2. Syngas sampling system

The first component in the syngas sampling system is an orifice with a diameter of 1 mm that limits the flow of gas into the syngas sampling system. A manually operated ball valve (MV-2G) is then used to control the gas flow rate into the syngas sampling system. The flow indicator FI-2G measures the flow rate of gas from the reactor into the sample vessel. Two ball valves (MV-4G and MV-7G) and two needle valves (MV-5G and MV-6G) are used to control the filling of the sample vessel and the purging of the sampling line. To reduce possible adsorption of H2S in the sample vessel it has been lined with Teflon.

2.2. Water cooling line

The water cooling line is connected to the burner cooling system which is an integral part of the PEHT-BLG process that is constantly monitored by the process control system. To measure the volume flow rate of cooling water into the probe a flow indicator (FI-1W) is used. After the flow indicator two ball valves are installed; the first one (MV-1W) is automatically controlled and the second one (AV-2W) is manually operated. A thermocouple (TC-2W) measures the temperature and a flow indicator (FI-2W) measures the flow rate of the outgoing water.

A difference between the two flow indicators FI-1W and FI-2W would indicate a leakage in the probe and in such an event, the two valves AV-1W and AV-2W will automatically close to ensure that no gas from the reactor can flow into the water cooling line. The valve AV-3W will also open so that dry nitrogen will flow into the water cooling passage and out through the leak. The pressure on the dry nitrogen is always 1 bar higher than the reactor pressure, thus ensuring a pressure gradient that will drive nitrogen into the reactor in case of leakage.

2.3. Gas sampling probe

Due to the harsh environment in the reactor the probe had to be designed to withstand both high temperature and severe corrosion. The probe and especially the tip had to be designed to avoid fouling and clogging by soot and to ensure rapid quenching of the sampled gas in order to obtain a representative sample of the gas composition inside the reactor. These issues are addressed and discussed in the following sections.

2.3.1. Mechanical considerations

The geometry of the gas sampling probe is presented in Fig. 3. The probe mainly consists of three concentric pipes (outer, middle and inner) with outer diameters of 30 mm, 18 mm and 8 mm, respectively. The wall thicknesses of the three pipes were 2.0 mm (outer), 2.0 mm (middle) and 1.5 mm (inner). Gas samples from the reactor were withdrawn through the inner pipe. At the probe tip an orifice with a diameter of 1.5 mm was formed. The purpose of the orifice is to limit the maximum possible mass flow rate of syngas and also, by creating the largest pressure drop in the gas sampling system close to the probe tip, to quench the sample gas by rapid expansion of the syngas downstream the orifice. The probe, made of stainless steel (SS-2333) was water cooled to reduce corrosion from direct contact with hot alkali smelt and the hot reducing conditions inside the reactor. The flow rate of cooling water was estimated from a heat balance calculation taking external convection and radiation from the hot gas and internal convection from the cooling water into account. It was found that the probe surface temperature is significantly dependent on the...
flow rate of cooling water (Fig. 4). Furthermore, the heat balance calculation performed in the initial system design phase showed that, using water as a cooling medium, the flow is sufficient to give a surface temperature of about 200°C, which is estimated to be enough to ensure the structural integrity of the probe.

When hot syngas is withdrawn through the probe, the length of the inner pipe will increase due to thermal expansion. To avoid large tensile stresses in the inner pipe the probe was constructed with a 90° bend (see Fig. 3). By doing so, the inner pipe can expand up to 9 mm corresponding to about a 900°C temperature increase before it is brought in contact with the outer pipe. The corresponding bending moment at the end of the probe where the inner pipe is welded to the outer pipe is for all practical purposes negligible.

2.3.2. Probe tip design

The initial probe sampling tests suffered from rapid clogging of the probe tip orifice. When this occurred the sampling experiment had to be stopped; the process plant shut down, the sampling probe removed, cleaned, and reinstalled; and the plant taken into operation again. All of these steps took approximately 24 h to perform. Hence, to prevent clogging, the probe tip was redesigned in several stages.

The smelt, which primarily consists of a binary mixture of Na₂CO₃ and Na₂S, has a melting behavior that depends on the smelt mixture composition [5, 6]. Pure Na₂CO₃ melts at a temperature of 858°C and pure Na₂S at a temperature of 1188°C. The eutectic point for a binary mixture of Na₂CO₃ and Na₂S is ~762°C and occurs for X_{Na₂S} of 0.4.

A flow visualization experiment using a water spray and a vacuum suction pump was conducted in order to get an illustration of the key features of the liquid smelt behavior close to the probe tip during gas sampling. The result then made it possible to redesign the probe tip to prevent clogging during the real experiments. Since the smelt has a viscosity similar to water at high temperature [7] it was believed that by using water as model liquid the real conditions inside the reactor could be properly simulated. The water spray experiments showed that great care has to be taken in the probe tip design, not only during suction (sampling) but also during purging between samples. Some of the tested probe tip configurations performed very well during suction but poorly during purging. This was mainly due to recirculation caused by the anti-clogging probe tip shields. From the water spray experiments it was found that two concentric holes and an anti-clogging probe tip shield with an angled piece shield at the end (see Fig. 5) gave good results with respect to separation of water from the gas during sampling and possible problems during purging.

The anti-clogging shield at the probe tip was designed so that the liquid smelt film formed on the top of the shield would not be convected to the inside of the shield. However, for this to work the probe shield temperature must be higher than the melting temperature for the smelt. If the anti-clogging shield is colder than the liquid smelt film it will freeze on the surface and thus eventually cause clogging.

On the other hand, keeping the tip hot would result in rapid corrosion that would destroy the shield in a few hours. This was also confirmed by real high temperature experiments in the gasifier where severe corrosion was seen on the anti-clogging shield. In one of the performed experiments the anti-clogging shield had corroded away completely when the probe tip was inspected after the experiment.

Even though the anti-clogging shield was designed to eliminate the problem of getting smelt film convected into the probe a small fraction of the film still will flow inside the shield, probably due to surface tension effects. This was recognized as one of the mechanisms that may still cause clogging. Even if the rate of entrainment of smelt into the shield is low it will eventually result in a pool of liquid smelt in the anti-clogging shield. The syngas will exert forces on this pool during suction that will force smelt towards the first orifice where it will freeze and cause clogging. Another potential mechanism that could cause clogging is small liquid smelt particles
that are entrained by the gas stream and will impact on the surface close to the first orifice where they will freeze and stick to the wall. Since the concentric hole configuration was chosen for the probe tip, and the experiments had exhibited good particle-gas separation, the aerodynamics in the probe were analyzed using the commercially available finite volume method based on CFD (Computational Fluid Dynamics) program, ANSYS CFX 11. The calculations were performed in order to confirm the intuitive results.

Fig. 6. Streamlines in the shielded probe tip during purging: Shield length $L = 50$ mm (a), shield length $L = 100$ mm (b). Flow is from right to left.

Fig. 7. Flow characteristics at the critical restriction. Flow is from left to right. (a) Contour plot of Mach number ($M$) up to $M < 0.1$. (b) Contour plot of Mach number. Solid line indicate $M = 1$. (c) Contours by temperature, line showing $M = 1$.1
about the behavior of the probe tip during suction and when purged with nitrogen. The simulations also yield information about the quenching effect from expansion of the gas from the reactor pressure to atmospheric pressure. The flow model was fully compressible with properties close to those for the expected gas mixture in the reactor. Turbulence was modeled using the k-ω turbulence model with scalable wall functions [8]. The boundary conditions (pressure in and pressure out) were set to the measured values during sampling and purging. The walls of the probe, including the anti-clogging shield, were treated as adiabatic.

During purging, the length of the anti-clogging shield (L in Fig. 5) played an important role: it had to be sufficiently long so that recirculation would not cause a transport of smelt into the shield. As can be seen in Fig. 6a when a shorter anti-clogging shield is used, there are three main eddies in the anti-clogging shield; the tip, the upper and the lower eddy. With a longer anti-clogging shield a plug flow at the probe tip is created (Fig. 6b) that suppresses the tip eddy that could potentially entrain and transport smelt into the shield.

During suction, the gas was accelerated through the shield, the first orifice and finally through the flow restrictor orifice. The average velocity in the anti-clogging shield was ~1.2 m/s (corresponding to a Mach number of 1.5 × 10^-3), and increased by a factor 50 at the first orifice (see Fig. 7a). Through the flow restrictor orifice the velocity was increased even further, reaching sonic conditions (Mach 1), with a strong shock diamond pattern at the exit from the orifice (Fig. 7b).

The rapid expansion in the orifice has an associated rapid temperature drop that will freeze any chemical reactions. Assuming isentropic expansion, a reactor pressure of 30 bar, a reactor temperature of 1000 °C, a nozzle downstream pressure of 1 bar and a syngas specific heat ratio (Cp/Cv) of 1.25, the gas temperature would be lowered approximately 350 °C due to the expansion. Similar results were seen in the simulations (Fig. 7c), a significant temperature drop as the gas is accelerated through the nozzle with local temperature drops of ~500 °C caused by the predicted shock-waves at the expansion. Since cooling due to wall heat flux was neglected in the CFD simulations, the temperature reaches the reactor temperature again after the expansion. To what extent the aerodynamic quenching is crucial for the probe performance is beyond the scope of the current work. However, gas sample experiments using the probe in the gasifier have showed that the thermo couple TC-2°C never exceeded 90 °C during sampling. This imply that the cooling rate is of the order of 10,000 °C/s, given the short residence time in the probe (Fig. 8).

3. Measurement procedure

To prevent contamination from previous gas samplings or from the atmosphere, the sample pressure vessel was purged with dry nitrogen prior to gas sampling. The pressure vessel was connected to the sampling system with needle valve MV-5° open and needle valve MV-6° closed. The valves MV-2°, MV-3° and MV-7° were opened sequentially and the flow rate of nitrogen through the sample pressure vessel was regulated manually with needle valve MV-6°, making sure that the pressure in the system did not drop below reactor pressure (see Fig. 8 point 1–2). The sample pressure vessel was purged ~30 s then needle valve MV-6° was closed together with valve MV-2°. The purging procedure was finished by opening and closing valve MV-4°, venting any syngas in the pressure release loop between valves MV-4° and MV-7°.

The gas sampling procedure is similar to the sample pressure vessel purging procedure. First, the nitrogen flow through the probe tip was turned off by closing ball valve MV-1° (Fig. 8, point 2). Thereafter, the ball and needle valves downstream MV-2° was opened (except MV-4°) so that syngas from the reactor could flow through the sampling line. The mass flow rate of syngas was controlled with the needle valve located after the pressure vessel (MV-6°). Practical tests showed that, a syngas flow of ~0.1 kg/min was sufficient to keep the residence time in the sampling line short and also, to avoid clogging of the nozzle (see Section 2.3.2 above). During the sampling procedure, the temperature downstream the probe (TC-2°C) increased rapidly and leveled out at ~60 °C when the mass flow rate of syngas had been adjusted to ~0.1 kg/min. Furthermore, during sampling the pressure in the sampling line after the probe (PG-1°) decreases to slightly above atmospheric pressure, indicating that the flow is choked at the probe tip orifice. The temperature increase and the flow rate of the cooling water to the probe indicated that the probe had a cooling power of ~3 kW. The pressure vessel and the sampling line were flushed with syngas for approximately 20 s after which the needle valve MV-6° was closed. When the pressure in the sampling line had reached reactor pressure, valve MV-6° was opened again for about 5 s and then closed (Fig. 8, point 3–4).

When the pressure in the vessel reached reactor pressure, needle valve MV-5° was closed. With the pressure vessel valves closed the system was ventilated to atmosphere by closing valve MV-2°C and opening valve MV-4°C. The nitrogen purge flow was turned on (Fig. 8, point 5) by opening valve MV-1° and the sample pressure vessel was removed from the gas sampling line and taken for gas analysis.

4. Experimental procedure

The probe was installed in the reactor before the start of the gasification process. There are two horizontal positions in the reactor where the probe tip can be installed. When the gasification process was stable, determined by monitoring the process control sensors, a gas sample from the reactor was taken according to Section 3. At the same time, syngas was collected after the DP-1 gas cooler (see Fig. 1) into a Tedlar bag so that the gas composition from the reactor was sampled with the probe described above could be compared with the gas composition after the gas cooler. After each gas sample the sample pressure vessel was moved to the ETC laboratory where the gas sample was analyzed with respect to CH4, CO, CO2, H2, N2, H2S, COS, and O2/Ar using a Varian CP-3800 gas chromatograph.

![Flow (Win/min) and temperature (°C)](image-url)
5. Results and discussion

Several measurement campaigns with the new sampling probe have been conducted in the gasifier. The left column plots in Fig. 9 shows the concentration of CO₂, CO, H₂, CH₄, H₂S and COS close to the outlet of the reactor obtained from the current high temperature gas sampling system and the sample obtained after the gas cooler during an experimental campaign performed in October 2008. Each data point corresponds to a certain combination of operational parameters. The aim with this measurement campaign was to investigate the gas composition at the exit from the reactor and to compare that gas composition with the gas composition after the gas cooler. The probe was therefore installed in the lower part of the DP-1 reactor, ~100 mm from the centerline and ~580 mm above the outlet which corresponds to 280 mm above the start of the straight pipe exit from the reactor (see Fig. 1). According to CFD simulations of reacting flow inside the hot reactor, the gas concentration in the lower part of the reactor where the probe is installed is homogeneous and one can therefore assume that the sampling point is representative for the syngas flow out from the reactor.

During the experimental campaign (7 October 15:30–10 October 17:10) 44 gas samples were withdrawn with the high temperature gas sampling system and several process parameters were varied systematically around a normal operation condition, both in the reactor and the quench. The normal operation was a reactor pressure of 27 bar and an oxygen/wet black liquor flow ratio (wt) of 0.29. The gasifier was repeatedly operated at normal operating conditions to determine the repetitiveness of the experimental conditions. The gas compositions from those measurements, that

![Fig. 9. Gas concentration measured with the high temperature gas sampling system close to the outlet but inside the hot reactor (r), and after the gas cooler (s). The left column shows all measurements (44 samples). The right column shows only repeatability measurements when the reactor is running at normal conditions (15 samples).](image-url)

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Average dry gas composition ± 1 standard deviation during normal operation condition of the gasifier.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Species</td>
<td>Probe measurements</td>
</tr>
<tr>
<td>CO₂ (% mole)</td>
<td>33.9 ± 0.3</td>
</tr>
<tr>
<td>CO (% mole)</td>
<td>28.7 ± 0.2</td>
</tr>
<tr>
<td>H₂ (% mole)</td>
<td>34.3 ± 0.2</td>
</tr>
<tr>
<td>CH₄ (% mole)</td>
<td>1.36 ± 0.07</td>
</tr>
<tr>
<td>H₂S (% mole)</td>
<td>1.65 ± 0.04</td>
</tr>
<tr>
<td>COS (ppm mole)</td>
<td>468 ± 22</td>
</tr>
</tbody>
</table>
should be identical if the operating conditions are identical, as shown in the right column in Fig. 9. Repeated measurements and subsequent analyses of the experimental data proved to be reproducible. The measurements also showed that the operating conditions had a significant influence on the gas composition. The average gas composition and the variation (±1 standard deviation) of the syngas during normal operating condition of the gasifier is summarised in Table 1. In general, the trends in gas composition of CO₂, CO, H₂, CH₄, and H₂S at the exit from the hot zone of the reactor and after the gas cooler follow each other relatively well. On the other hand, COS undergoes a significant reduction during the passage from gas cooler follow each other relatively well. On the other hand, COS undergoes a significant reduction during the passage from gas cooler to the exit from the reactor compared to the CH₄ concentration after the gas cooler is of special interest. The concentration of CH₄ can be regarded as relatively inert when the temperature of the gas is rapidly reduced in the quench. The concentration of the other components can be affected due to chemical reactions and/or absorption in the water sprays or the green liquor bath. As an example, the proportions between CO, H₂O, H₂, and CO₂ can be altered by the water gas shift reaction [9]

$$\text{CO} + \text{H₂O} \rightarrow \text{H₂} + \text{CO₂}$$

where the syngas temperature is reduced and the partial pressure of water vapor is increased due to introduction of water spray in the quench. Furthermore, the concentration of CO₂, H₂S and COS may be reduced due to absorption in the water sprays and the green liquor bath. The concentration of CH₄ measured with the probe was the same as the CH₄ concentration after the gas cooler. Therefore, it is likely that the reaction in the probe tip is adequately suppressed by gas quenching since without the quenching CH₄ would be converted to CO and H₂ in a high temperature reaction with H₂O [9] in the probe

$$\text{CH₄} + \text{H₂O} \rightarrow \text{CO} + 3\text{H₂}$$

In all measurements (see Fig. 9), the CH₄ concentration out from the reactor measured with the high temperature sampling system and in the syngas after the gas cooler follow each other and are almost identical. This indicates that the fast quenching rate in the probe tip (∼10,000 °C/s) was fast enough to freeze all reactions of CH₄ and that the measured CH₄ concentration is representative of the CH₄ concentration in the lower part of the hot reactor. For the major gas components H₂, CO, and CO₂ it is more difficult to prove that the measured gas composition represents the true gas composition inside the reactor. The main difficulty is that these species can undergo further changes as a result of the water-gas shift reaction both after the hot reactor and inside the high temperature gas sampling probe. Thus, it is not reliable to make a direct comparison of the measured gas composition with the high temperature gas sampling probe and with measurements on cooled raw gas. However, given the large differences between the estimated quenching rate (∼10,000 °C/s) and the reaction rate for the water-gas shift reaction (∼10 mol m⁻³ s⁻¹ at 1273 K) [10], it is unlikely that the water-gas shift reaction will notably alter the concentrations of the major gas component obtained by the high temperature gas sampling probe.

The aim with the present paper was to evaluate the performance of the high temperature gas sampling system described above. The effect of different process parameters on the syngas composition, as shown in Fig. 9, is therefore not discussed further in this paper. However, this will be evaluated in an on-going work by our research group [11,12]. Fig. 10a is a photography of the probe after the experiment. It is surprising that, for the majority of cases, no significant amount of smelt could be found on the cooled surface of the probe, only a thin layer of carbonized material (solid carbon) could be seen. After cleaning, no attack from corrosion could be seen on the cooled surface of the probe. There are at least two possible explanations for this phenomenon. (i) It is likely that during the gasification process, solid carbon is formed on the surface of the probe from the syngas. The properties of the solid carbon deposit prevent liquid smelt droplets to stick to the probe surface and the droplet will fall off the probe instead. (ii) The other explanation is that the radiation from the cooled surface is sufficient to cool approaching smelt droplets below the melting point and thereby make them non-sticky before they get in contact with the probe surface. As can be seen in Fig. 10b, the un-cooled probe tip suffers both from deposits and corrosion from the smelt.

6. Conclusion and further work

The following conclusions could be drawn from this work:

- A water jacketed cooled sampling probe will survive the conditions inside the reactor in a PEHT-BLG plant for a long time.
- Smelt droplets will not stick to the cooled surface of the probe but on the un-cooled part of the probe deposits will form and corrosion of the stainless steel will be severe.
- Syngas could be withdrawn from the hot reactor with the gas sampling system without jeopardizing the safety of the operators.
- During sampling, the most crucial part is to avoid clogging of the probe tip. This could be done by an appropriate design of the probe tip.
- The measurement of the gas composition was fully reproducible and a significant effect on the gas composition from different operating parameters of the gasifier was discovered.
In the planned future work, the high temperature gas sampling system will be developed to also measure gas temperature, condensable species and fumes in the gas stream.

Acknowledgement

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References

Paper II

Experimental investigation of an industrial scale black liquor gasifier. 1. The effect of reactor operation parameters on product gas composition

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A B S T R A C T

A novel technology to mitigate the climate changes and improve energy security is Pressurized Entrained Flow High Temperature Black Liquor Gasification (PEHT-BLG) in combination with an efficient fuel synthesis using the resulting syngas [1]. Black liquor is a by-product in the chemical Kraft pulping process [2] where wood chips are fed into a digester and white liquor (water solution of the cooking chemicals) dissolves the lignin that bonds the cellulose fibers. The cellulose fibers are then separated from the lignin and the cooking chemicals to form pulp that can be used for paper production. The remaining solution, consisting of the spent cooking chemicals, water and the separated lignin is referred to as weak liquor. The weak liquor is turned into black liquor by passing the solution through several evaporation units raising the dry content from approximately 15% to up to about 75%. The objectives with the PEHT-BLG process are to efficiently produce a high caloric value product gas, rich in H2 and CO, from the direct gasification step and to form well composed regenerable cooking chemicals in form of high quality green liquor from the inorganic ash part of the black liquor. The input fuel to the gasification plant comes in form of high quality green liquor from the inorganic ash part of the black liquor. The input fuel to the gasification plant comes from biomass, hence, the net CO2 contribution to the atmosphere is vanishingly small compared to products derived from e.g. coal gasification [3]. An additional benefit is that the process will be integrated in a pulp mill which has well established infrastructure to handle biomass and chemicals.

Combustion and gasification characteristics of black liquor in lab-scale have been investigated by several authors [4–10]. However, to the authors’ knowledge, no analyses have been conducted with samples taken inside an industrial size gasification reactor for PEHT-BLG. In this work, the local gas composition inside such a reactor has been measured through the use of a water cooled gas sampling system [11]. The process conditions; pressure, temperature, residence time and level of atomization have been affected by varying the operational parameters; black liquor to oxygen equivalence ratio (defined as \( k = \frac{x_{O2}}{(x_{O2} + x_{H2})/x_{H2}} \)), where \( x \) is the mole fraction, black liquor flow rate to pressure ratio and black liquor pre-heat temperature. Due to the harsh environment inside the gasification reactor, gas sampling is a challenging task. However, for the purpose of the current study, a specially designed high temperature gas sampling system was successfully developed and used. The results, obtained from two separate experimental campaigns, show that all of the investigated operational parameters have a significant influence on the product gas composition and present valuable information about to the process characteristics.

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1. Introduction

Among the current efforts to mitigate the climate changes and improve energy security, efficient production of bio based motor fuels is of great importance. A novel technology to achieve this is Pressurized Entrained Flow High Temperature Black Liquor Gasification (PEHT-BLG) in combination with an efficient fuel synthesis using the resulting syngas [1]. Black liquor is a by-product in the chemical Kraft pulping process [2] where wood chips are fed into a digester and white liquor (water solution of the cooking chemicals Na2S and NaOH) dissolves the lignin that bonds the cellulose a digester and white liquor (water solution of the cooking chemicals Kraft pulping process [2] where wood chips are fed into a digester and white liquor (water solution of the cooking chemicals Na2S and NaOH) dissolves the lignin that bonds the cellulose and to form well composed regenerable cooking chemicals in form of high quality green liquor from the inorganic ash part of the black liquor. The input fuel to the gasification plant comes from biomass, hence, the net CO2 contribution to the atmosphere is vanishingly small compared to products derived from e.g. coal gasification [3]. An additional benefit is that the process will be integrated in a pulp mill which has well established infrastructure to handle biomass and chemicals.

Combustion and gasification characteristics of black liquor in lab-scale have been investigated by several authors [4–10]. However, to the authors’ knowledge, no analyses have been conducted with samples taken inside an industrial size gasification reactor for PEHT-BLG. In this work, the local gas composition inside such a reactor has been measured through the use of a water cooled gas sampling system [11]. The process conditions; pressure, temperature, residence time and level of atomization have been affected by varying the operational parameters; black liquor to oxygen equivalence ratio (defined as \( k = \frac{x_{O2}}{(x_{O2} + x_{H2})/x_{H2}} \)), where \( x \) is the mole fraction, black liquor flow rate to pressure ratio and black liquor pre-heat temperature. Depending on if the product gas is intended as fuel in a gas engine/turbine or as feedstock in a catalytic process aimed for motor fuel production (fuel synthesis) the criterion regarding gas
composition is different. If used as fuel in a gas engine, a high cal-
corific heating value is desired. Hence, CH₄ presents no problem.
However, in catalytic conversion CH₄ is not an active compound,
which means that it can become enriched through recirculation
in the synthesis plant and thus reduce its efficiency. H₂S and COS
are undesired in both processes. These gas components deactivate
catalysts[12] thus adding costs to the catalyst plant and reduced
reactor samples and the obtained results are evaluated with re-
respect to quench performance, as feedstock to a synthesis plant
and fuel for a gas engine/turbine.
The main objective with this work is, to evaluate the perfor-
mance of an industrial size PEHT-BLG reactor with respect to gas
composition under different operational conditions. Furthermore,
the results are intended to give valuable insights concerning optimi-
ization of the process operation and provide a base for validation and
improvement of existing Computational Fluid Dynamics-models
[14].

1.1. Process overview

The considered PEHT-BLG plant in the present paper was the
industrial so called Development Plant-1 (DP-1) schematically pre-
sented in Fig. 1. The plant is owned and operated by Chemrec AB
(first commissioned in October 2005) and has a nominal capacity of
20 ton/day of black liquor (as dry solids), corresponding to
approximately 3 MW thermal throughput[1]. The main parts of
the plant are: a slagging refractory lined entrained flow gasification
reactor (2.3 m in height and 0.6 m in inner diameter) used for di-
rect gasification of the black liquor at about 1000 °C and 30 bar
(g) to produce a product gas and a liquid smelt; a quench cooler be-
neath the reactor where the product gas and smelt are separated
from each other and the smelt is dissolved in water forming green
liquor; a Counter Current Condenser (CCC) that cools the steam
saturated product gas and condenses the water vapor and any
other condensable species that may be present.
The heat recovered from the gas condensation can be used to
generate low/medium pressure steam that can be used in the pulp
and paper process. Furthermore, the spent cooking chemicals from
the black liquor are partly regenerated in the quench and recycled
back to the mill as green liquor. Compared to a bench-scale gasifier,
all equipments in the DP-1 comply with industrial standards;
however, the experiments conducted in this work are not idealized,
instead they may serve as a benchmark for how the product gas
composition can be altered by changing some of the operational
parameters in a fully industrialized PEHT-BLG plant.

As a fuel, black liquor differs significantly from coal and solid
biomass (see Table 1). It is characterized by a high water and ash
content, where the ash mainly consists of spent cooking chemicals
in the form of different sodium and sulphur compounds (called
smelt at high temperature) and low levels of ash from the pulp
wood[2].

In the entrained flow gasification reactor of the PEHT-BLG pro-
cess, pre-heated black liquor is centrally introduced at the reactor
top via a gas assisted burner nozzle producing a fine spray of drop-
lets and ligaments [17] with a characteristic diameter of the order
~100 μm. As the atomized black liquor pass through the gasifica-
tion reactor, the black liquor undergo four stages of conversion
[4,18]: drying, devolatilization, char gasification and smelt forma-
tion (see Fig. 2). During the conversion, the morphology of the
droplets undergoes a significant change of which swelling is most
predominant[8]. The conversion stages mainly occur sequentially,
one after another, but may also overlap [4].

During the different conversion stages there is a large net mass
transfer from the black liquor to the gas phase. During drying, the

Table 1

Proximate and ultimate analysis for typical northern Sweden black liquor [14], bituminous coal [15], and pine [16].

<table>
<thead>
<tr>
<th></th>
<th>Black Liquor %wt</th>
<th>Bituminous Coal %wt</th>
<th>Pine %wt</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
<td></td>
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<tr>
<td>Moisture</td>
<td>28.0</td>
<td>13.0</td>
<td>12.9</td>
</tr>
<tr>
<td>Volatiles</td>
<td>29.5</td>
<td>37.0</td>
<td>71.5</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>8.5</td>
<td>39.3</td>
<td>15.3</td>
</tr>
<tr>
<td>Ash</td>
<td>34.0</td>
<td>10.7</td>
<td>0.3</td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>34.9</td>
<td>78.4</td>
<td>41.9</td>
</tr>
<tr>
<td>H</td>
<td>3.4</td>
<td>5.4</td>
<td>4.5</td>
</tr>
<tr>
<td>O</td>
<td>35.1</td>
<td>9.9</td>
<td>80.2</td>
</tr>
<tr>
<td>N</td>
<td>&lt;0.1</td>
<td>1.4</td>
<td>0.2</td>
</tr>
<tr>
<td>S</td>
<td>5.0</td>
<td>4.9</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Na</td>
<td>19.4</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>K</td>
<td>2.2</td>
<td>&lt;0.2</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td><strong>LHV MJ/kg</strong></td>
<td>13.1</td>
<td>35.7</td>
<td>16.8</td>
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</table>
Table 2  Main global reactions in the black liquor gasification reactor.  

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
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<tbody>
<tr>
<td>1</td>
<td>H₂O(l) → H₂(g)</td>
</tr>
<tr>
<td>2</td>
<td>H₂ + ½ O₂ → H₂O</td>
</tr>
<tr>
<td>3</td>
<td>CO + ½ O₂ → CO₂</td>
</tr>
<tr>
<td>4</td>
<td>CH₄ + ½ O₂ → 2H₂O</td>
</tr>
<tr>
<td>5</td>
<td>CO₂ + SO₂ → CO₂ + 2H₂O</td>
</tr>
<tr>
<td>6</td>
<td>H₂S + O₂ → SO₂ + H₂</td>
</tr>
<tr>
<td>7</td>
<td>CO₂ + O₂ → 2CO</td>
</tr>
<tr>
<td>8</td>
<td>C₇H₈O₃ + 8O₂ → 7CO₂ + 4H₂O</td>
</tr>
<tr>
<td>9</td>
<td>C₂H₄O₂ + 4O₂ → 2CO₂ + 2H₂O</td>
</tr>
<tr>
<td>10</td>
<td>CO + H₂O → CO₂ + H₂</td>
</tr>
<tr>
<td>11</td>
<td>CO₂ + H₂O → CO + H₂O</td>
</tr>
<tr>
<td>12</td>
<td>CO + H₂ + CO₂ + H₂S</td>
</tr>
<tr>
<td>13</td>
<td>SO₂ + H₂S → 2H₂O + H₂S</td>
</tr>
<tr>
<td>14</td>
<td>CO + 2O₂ → CO₂</td>
</tr>
<tr>
<td>15</td>
<td>C + H₂O → CO + H₂</td>
</tr>
<tr>
<td>16</td>
<td>C + 2H₂ → CH₄</td>
</tr>
<tr>
<td>17</td>
<td>C + ½ O₂ → CO</td>
</tr>
<tr>
<td>18</td>
<td>C + ½ O₂ → CO₂</td>
</tr>
<tr>
<td>19</td>
<td>C + Na₂SO₄(l) → Na₂S + CO₂</td>
</tr>
<tr>
<td>20</td>
<td>2NaOH(l) + CO₂ → Na₂CO₃(1) + H₂O</td>
</tr>
<tr>
<td>21</td>
<td>Na₂CO₃(l) + H₂O + CO₂ → Na₂CO₃(1) + H₂S</td>
</tr>
<tr>
<td>22</td>
<td>Na₂CO₃(l) + 2O₂ → Na₂SO₄(l) + CO₂</td>
</tr>
</tbody>
</table>
and October 2008 where the focus was on four specific process conditions: reactor pressure, reactor temperature, residence time and level of black liquor atomization. These process conditions were varied systematically by changing the operational parameters: system pressure, black liquor to oxygen equivalence ratio \( \left( \frac{x}{1-x} = \frac{\text{O}_2}{\text{black liquor}} \right) \), black liquor flow rate to system pressure ratio (explained below), and black liquor pre-heat temperature. The operational parameter values for the “base case” in the two experimental campaigns are presented in Table 3 together with an ultimate analysis for the black liquor used in each campaign. There were differences between the black liquor used in the May and October campaign. Particularly, the sulphur content was approximately 10% higher in the October campaign compared to the May campaign. For C, H, O, N, Na and K the difference was within 7.5%. The difference in the October campaign compared to the May campaign. For C, H, O, N, Na and K the difference was within 7.5%. The difference in the October campaign compared to the May campaign. For C, H, O, N, Na and K the difference was within 7.5%.

Table 3 Reactor base operating parameters and ultimate analysis for May 2008 and October 2008 campaign.

<table>
<thead>
<tr>
<th>Variable</th>
<th>May</th>
<th>October</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>30</td>
<td>27</td>
<td>bar</td>
</tr>
<tr>
<td>Black liquor mass flow rate</td>
<td>1250</td>
<td>870</td>
<td>kg h⁻¹</td>
</tr>
<tr>
<td>( \text{O}_2 ) mass flow rate</td>
<td>375</td>
<td>254</td>
<td>kg h⁻¹</td>
</tr>
<tr>
<td>Black liquor temperature</td>
<td>140</td>
<td>140</td>
<td>°C</td>
</tr>
<tr>
<td>( \text{O}_2 ) temperature</td>
<td>50</td>
<td>50</td>
<td>°C</td>
</tr>
<tr>
<td>x</td>
<td>0.42</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>BLP</td>
<td>41.67</td>
<td>32.22</td>
<td>kg h⁻¹ bar⁻¹</td>
</tr>
<tr>
<td>Black liquor ultimate analysis (on dry sample)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>13.8</td>
<td>31.3</td>
<td>%wt</td>
</tr>
<tr>
<td>H</td>
<td>3.6</td>
<td>1.4</td>
<td>%wt</td>
</tr>
<tr>
<td>O</td>
<td>31.1</td>
<td>37.3</td>
<td>%wt</td>
</tr>
<tr>
<td>N</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>%wt</td>
</tr>
<tr>
<td>S</td>
<td>1.1</td>
<td>5.6</td>
<td>%wt</td>
</tr>
<tr>
<td>Na</td>
<td>20.2</td>
<td>20.1</td>
<td>%wt</td>
</tr>
<tr>
<td>K</td>
<td>2.2</td>
<td>2.3</td>
<td>%wt</td>
</tr>
<tr>
<td>HHV</td>
<td>13.37</td>
<td>12.57</td>
<td>MJ kg⁻¹</td>
</tr>
</tbody>
</table>

The residence time of the gas through the reactor will depend on the total mass flow rate (black liquor and oxygen) going into the reactor. An increase of mass flow rate will result in higher inlet velocities thus shortening the residence time for a fixed pressure. An increase of pressure will have the opposite effect; increasing the gas residence time. In Eq. (1) the relation is summarized, based on an assumption of uniform plug flow in the reactor.

\[
\frac{m}{\rho} = \frac{\pi}{2v} \Rightarrow \tau = \frac{\pi}{4} \frac{\rho}{\rho_{\text{sys}}} \left( \frac{\rho_{\text{sys}}}{\rho_{\text{fuel}}} \frac{L}{\tau} \right) \tag{1}
\]

Here, \( m \) is the mass flow rate of black liquor and oxygen, \( A \) is the reactor cross-sectional area (main cylindrical part), \( v \) is the plug flow velocity, \( \rho \) is the gas density, \( L \) is the reactor length, \( \tau \) is the residence time, \( P \) is the system pressure, \( \rho_{\text{sys}} \) is the specific gas constant \( (R = R/M) \) and \( T \) temperature.

Since the black liquor contains approximately one third of inorganic ash and cooking chemicals with a high boiling temperature, only two thirds of the available black liquor will be converted to gas. Hence, to calculate the residence time based on the plug flow
assumption described in Eq. (1) the black liquor mass flow rate needs to be compensated. However, the mass flow rate of steam is of the same order as the mass flow rate of oxygen. For this reason, instead of compensating the black liquor mass flow rate for smelt content, the black liquor mass flow rate was used, unmodified, in Eq. (1) and the oxygen mass flow rate was ignored. Hence, instead of compensating the black liquor mass flow rate for the residence time, the black liquor is atomized \[17\]. The extra sensible heat input was expected, which results in a smaller droplet size distribution when the black liquor temperature from 140 °C is increased \[19\] as well as a decrease in surface tension \[20\] are expected. This is important for variations in the black liquor pre-heating temperature because of the smaller droplet size distribution when the black liquor is atomized \[17\]. The extra sensible heat input by the increased black liquor temperature from 115 to 150 °C was calculated to be approximately 30 kW, which corresponds to one third of the estimated wall heat loss. In the May campaign the influence of black liquor pre-heating temperature on gas composition was investigated in a similar fashion by reducing the black liquor temperature from 140 °C (base case) to 120 °C (see Table 7).

### 3. Results

The results presented below include the measured gas composition for variations in reactor pressure, oxygen to black liquor equivalence ratio, BLP and black liquor pre-heating temperature. All gas samples were withdrawn from the reactor using the high temperature gas sampling system described in Section 2.1. Since there are variations in the black liquor composition and thermal throughput between the May and October campaigns (see Table 3), the results from these two campaigns are presented separately. The gas composition presented in the paragraphs below are on molar basis as dry and nitrogen free together with the lower heating value LHV in MJ/kg calculated from the measured gas composition.

#### 3.1. Effects from variation of the system pressure

Similar trends were observed in the May and October campaign when investigating the influence of system pressure on local gas composition (see Fig. 4). In both cases a reduction of CO2 and an increase of CO and H2 were observed when the pressure was

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Pressure (bar)</th>
<th>( \lambda )</th>
<th>BLP (kg h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>20</td>
<td>0.44</td>
<td>41.50</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.44</td>
<td>41.67</td>
</tr>
<tr>
<td>October</td>
<td>27</td>
<td>0.39</td>
<td>32.22</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.44</td>
<td>32.22</td>
</tr>
</tbody>
</table>

#### Table 5 Operating parameters when investigating the influence of oxygen to black liquor equivalence ratio on local gas composition.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Pressure (bar)</th>
<th>( \lambda )</th>
<th>BLP (kg h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>20</td>
<td>0.44</td>
<td>41.50</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.44</td>
<td>41.67</td>
</tr>
<tr>
<td>October</td>
<td>27</td>
<td>0.39</td>
<td>32.22</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.44</td>
<td>32.22</td>
</tr>
</tbody>
</table>

#### Table 6 Operating parameters when investigating the influence of residence time on local gas composition.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Pressure (bar)</th>
<th>( \lambda )</th>
<th>Black liquor temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>30</td>
<td>0.42</td>
<td>41.67</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.42</td>
<td>41.67</td>
</tr>
<tr>
<td>October</td>
<td>27</td>
<td>0.44</td>
<td>32.22</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.44</td>
<td>32.22</td>
</tr>
</tbody>
</table>

#### Table 7 Operating parameters when investigating the influence of black liquor pre-heating temperature on local gas composition.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Pressure (bar)</th>
<th>( \lambda )</th>
<th>BLP (kg h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>20</td>
<td>0.44</td>
<td>41.50</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.44</td>
<td>41.67</td>
</tr>
<tr>
<td>October</td>
<td>27</td>
<td>0.44</td>
<td>32.22</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.44</td>
<td>32.22</td>
</tr>
</tbody>
</table>

#### 2.3. Overview of operating conditions in the experiments

The effect of reactor pressure was investigated by running the DP-1 plant at five different system pressures: 15, 20, 25, 27 and 30 bar (g). During the experiments the temperature inside the reactor was held constant at around 1050 °C by changing the system pressure due to reasons explained below. In Table 4, the system pressure, oxygen to black liquor equivalence ratio and BLP for the May and October campaign are summarized. Notice that the BLP is nearly constant for the runs within each of the individual campaigns but differ significantly between the two considered campaigns. The reduction of the BLP in the October campaign is due to a change in base operating parameters decided by the owner of the plant. Since the wall heat losses (estimated to approximately 90 kW) will be a greater portion of the total thermal throughput at reduced pressure (and consequently reduced black liquor flow rate), \( \lambda \) was slightly increased at reduced pressure in order to maintain a constant reactor temperature.

By varying the oxygen to black liquor equivalence ratio from 0.39 to 0.45 the temperature inside the reactor was changed from 1020 °C to 1080 °C in the October campaign. During the measurements, system pressure and BLP were held constant at 27 bar (g) and 32.2 kg h\(^{-1}\) bar\(^{-1}\), respectively. In the May campaign similar variations were done but at a different pressure and BLP (see Table 5).

In the October campaign, BLP was changed from about 16 to 50 kg h\(^{-1}\) bar\(^{-1}\), these variations were made by changing both the black liquor flow rate and the system pressure. In the May campaign the system pressure was held constant at 20 bar (g) whilst the black liquor flow rate was varied to achieve a corresponding change in BLP (see Table 6). The pre-heating temperature of black liquor was systematically varied around normal operating conditions. In the October campaign the black liquor pre-heating temperature was varied between 115 and 150 °C, which can be compared with the base case temperature of 140 °C. In this temperature range a significant viscosity decrease \[19\] as well as a decrease in surface tension \[20\] are expected, which results in a smaller droplet size distribution when the black liquor is atomized \[17\].

#### Table 4 Operating parameters when investigating the influence of pressure on local gas composition.

<table>
<thead>
<tr>
<th>Campaign</th>
<th>Pressure (bar)</th>
<th>( \lambda )</th>
<th>BLP (kg h(^{-1}) bar(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>May</td>
<td>15</td>
<td>0.45</td>
<td>41.67</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.44</td>
<td>41.50</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.43</td>
<td>41.56</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.42</td>
<td>41.73</td>
</tr>
<tr>
<td>October</td>
<td>15</td>
<td>0.46</td>
<td>32.47</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>0.46</td>
<td>32.25</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>0.44</td>
<td>32.22</td>
</tr>
</tbody>
</table>
increased. For CH₄, H₂S and COS, which in this work are referred to as minor gases, an increase in system pressure resulted in higher concentrations of each of these species, except for CH₄ in the May campaign, when its concentration was almost constant.

There is also an influence from variations in the oxygen to black liquor equivalence ratio in the system pressure variation experiments as can be seen in Fig. 4. At a reduced system pressure, and a correspondingly reduced mass flow rate of black liquor, additional oxygen was used to compensate the wall heat losses which can be seen as a decrease in heating value at increased λ.

3.2. Effects from variation of the oxygen to black liquor equivalence ratio

Even though some differences can be seen for all gas components (Fig. 5) when the oxygen to black liquor equivalence ratio is varied, the most significant difference is found for CH₄. In the May campaign (Fig. 5b), CH₄ is reduced from 2.75% to 0.90% when the oxygen to black liquor ratio is increased from 0.29 to 0.31, which corresponds to an oxygen to black liquor equivalence ratio of 0.40 and 0.44, respectively. Similar effects can be seen in the October campaign (Fig. 5d) when CH₄ decreased from 2.72% to 0.76% when the oxygen to black liquor equivalence ratio was changed from approximately 1020 °C to 1080 °C during these variations. For the bulk gas components (CO₂, CO and H₂), the increase of CO with increasing λ is the most dominant effect both in the May and October campaign. It is also possible to distinguish a reduction of H₂ and an increase of CO₂ in the October campaign when λ is increased. As in the pressure variation experiments, the heating value decreases significantly with increased oxygen to black liquor equivalence ratio.

3.3. Effects from variation of the residence time

Both in the May and October campaign the CO₂ concentration decreased with decreasing residence time, i.e. increased BLP (see Figs. 6 and 7). In May, the CO₂ content in the gas was reduced from 34% to 31%. In October similar trends were seen in form of a reduction of CO₂ content from approximately 37% to 35% at 20 bar (g) pressure, and from 37% to 34% at 30 bar (g) pressure (see Fig. 7a and c).

As the residence time was decreased, i.e. BLP increased, the H₂ and CH₄ content in the gas increased for both campaigns (see Figs. 6 and 7). In the October campaign, the CO content was close to 27% at 20 bar (g) reactor pressure (see Fig. 7a) almost independent of residence time. At a system pressure of 30 bar (g) the CO content was again almost constant, expect for the case with the shortest residence time (BLP = 33.33 kg h⁻¹ bar⁻¹) when the CO level decreased. In the May campaign, the CO content in the gas increased from approximately 29% to 30.5% when the residence time was reduced. For H₂S the content in the gas seems to be unaffected by the residence time in both the October campaign (Fig. 7b and d) and in the May campaign (Fig. 6b). However, COS showed very large variations in the October campaign and a small increase with reduced residence time in the May campaign. The heating value increased with increased BLP, i.e. decreased residence time for both campaigns.

3.4. Effects from variation of the black liquor pre-heat temperature

Compared to the influence of system pressure, oxygen to black liquor equivalence ratio, and residence time the effect black liquor pre-heat temperature shows very little influence on the composition for the bulk gas components (Fig. 8a and c). However, for the minor gases (Fig. 8b and d) a reduction can be seen for all
components when the black liquor pre-heat temperature is increased. In particular, CH4 shows a substantial decrease in the investigated temperature range. In the May campaign the heating value decreased from 8.21 to 8.07 MJ/kg for a corresponding black liquor pre-heat temperature of 120–145°C, respectively. For the October campaign the heating value varied between 7.39 and 7.50 MJ/kg with no apparent coupling to the black liquor pre-heat temperature.

4. Discussion

At low reactor load, i.e. low black liquor flow rate, the wall heat losses will play a larger role in the heat balance for the reactor. Hence, to maintain constant temperature at decreased reactor load, the oxygen to black liquor equivalence ratio needs to be increased. Consequently, at low black liquor flow rates the CO2 content in the gas will increase since more CO, CH4 and H2 will be combusted to CO2 and H2O. This effect can be seen both in the pressure variation experiments (Fig. 4) and in the residence time experiments conducted in October (Fig. 7). However, if the reactor load is kept constant and the oxygen to black liquor equivalence ratio is increased the temperature in the reactor will increase. The resulting bulk gas composition (Fig. 5) will then be determined by both the temperature increase and a displacement of the water gas CO-shift reaction (Table 2, reaction 10) moving it towards left, i.e. more CO and H2O due to the increased amount of added oxygen.

In the system pressure variation experiments (Fig. 4), the CO2 content in the gas decreased with increased pressure. The decrease is most likely an affect of the decrease of oxygen to black liquor
Fig. 7. Residence time influence on gas composition; (a) bulk gas composition and (b) minor gas composition for October campaign at 20 bar (g) reactor pressure. (c) Bulk gas composition and (d) minor gas composition for October campaign at 30 bar (g) reactor pressure. Lower heating value (LHV) in MJ/kg.

Fig. 8. Black liquor pre-heat temperature influence on gas composition; (a) bulk gas composition and (b) minor gas composition for May campaign at. (c) Bulk gas composition and (d) minor gas composition for October campaign. Lower heating value (LHV) in MJ/kg.
equivalence ratio in these experiments. Also, the increase of CO and H₂ can be related to the decrease of oxygen to black liquor equivalence ratio. However, an alternative interpretation of the experimental results from pressure changes is that more CO₂ absorbs into the smelt forming Na₂CO₃, H₂S and COS according to reactions 21 and 22 to a larger extent at elevated pressures (reactions 21 and 22 shift towards right at increased pressure), the H₂S and COS content increase significantly as pressure increase which could support this. Apart from this, no significant system pressure dependency can be detected. The weak pressure dependency is expected since; the main reaction determining the bulk gas composition appears to be the water gas CO-shift reaction (reaction 10) which has no pressure dependency according to the Chatelet’s principle. On the other hand, the steam methane reforming reaction has a pressure dependency where an increased pressure will shift the equilibrium towards the side with fewer moles (reaction 11 towards left). However, it is possible that; given the short residence time in the reactor and the relatively slow kinetics for the reaction explains why a pressure dependency is not detected.

When j is increased at constant pressure (Fig. 5), the heating value of the gas decreased approximately 6% in the May campaign and 10% in the October campaign when j was increased. However, if CH₄ is considered inert the heating value is almost constant in the May campaign with a reduction of only 0.25%. In the October campaign the reduction in heating value was 3% if CH₄ was considered inert. Hence, if the gas is intended as feedstock to a fuel synthesis plant a significant amount of the CH₄ can be converted to active components (CO, H₂) in the gasifier without reducing the heating value of the gas considerably.

The BLP was used as a single measure of reactor residence time. However, it could also be interpreted as a measure of gasifier flow characteristics. An exceedingly low BLP (low black liquor flow rate, high pressure) results in low velocities in the reactor which could alter the flow field or turbulent mixing rate compared to a high BLP. It is possible that the presumed recirculation zones may be less well established, i.e. shorter and weaker in a low BLP case. Still, the BLP has an influence on the gas composition. The October experiment conducted at 20 bar (g) system pressure (see Fig. 7a and b) had very small variations in j and hence, the variations in the gas composition can most probably be explained by the variations in BLP. In the experiments it is possible to distinguish an increase in heating value of the gas at elevated BLP. Similarly, a reduction of the CO₂ content in the gas is observed at elevated BLP. As BLP was increased a reduction of analyzed carbon containing gases was observed. In the October experiment conducted at 20 bar (g) system pressure the reduction was from 65.75% to 63.84% with a corresponding BLP of 24.25 and 50.00 kg h⁻¹ bar⁻¹, respectively. It is possible that the reduction is directly related to the residence time. That is, given a longer residence time, non-analyzed carbon containing species (char, soot, condensable species and gases) are converted to a larger extent, which could explain the increase of carbon in the gas. Interestingly, the heating value of the analyzed gas increase consistently with increased BLP both in the May and October campaign. Even though CH₄ concentrations increase with increased BLP the increase in heating value can not be explained by this alone. For example, in the October campaign conducted at a pressure of 20 bar (g) which is shown in Fig. 7a and b; if CH₄ is treated as inert the heating value of the gas increase from 6.55 to 6.97 MJ/kg with a corresponding BLP of 24.25 and 50.00 kg h⁻¹ bar⁻¹, respectively. Hence, the black liquor flow rate to pressure ratio influence the heating value of the bulk gas. This could be an effect of mixing, i.e. at a high BLP; turbulent mixing would be more intense and consequently, reactions would evolve faster towards equilibrium. On the other hand, the increase in BLP would also result in a reduced residence time. However, the increasing heating value of the gas with increasing BLP indicates that the increase in turbulent mixing is dominating over the decrease in residence time.

When the black liquor pre-heat temperature is increased, it is believed that the change in concentration for the bulk gases is mainly caused by the increased thermal input to the gasifier (approximately 30 kW). This results in a temperature increase in the reactor (Fig. 8). However, as showed by Risberg and Marklund [17] increasing the black liquor pre-heating temperature will result in smaller droplet size distributions from the gas assisted spray nozzle. Smaller droplets will be subjected to higher heating rates in the gasifier, which in turn can alter the composition of the volatile species released during pyrolysis. Sricharoenchaikul et al. [5] showed that higher temperature, i.e. high heating rate, during conversion of small black liquor particles promotes semi volatile species at short residence time. It was also discovered that the semi volatile species decreased rapidly with increased residence time. Assuming that CH₄ can be used as an indication of the presence of heavier hydrocarbons it is possible that, increased black liquor pre-heat temperature results in higher heating rates which in turn gives longer residence time at high temperature (flame region) for the pyrolysis products. Thus, the conversion (through reactions 8 and 9) of large hydrocarbons released during pyrolysis is higher if the black liquor pre-heat temperature is increased. This could possibly explain the reduction of CH₄ that is observed in the two experimental campaigns.

A similar line of thought can be used to explain the small reduction of H₂S with elevated black liquor pre-heating temperature. A higher heating rate could promote sulphur to be bound as Na₂S and Na₂SO₄ in the droplet [21] instead of being released as H₂S and COS due to kinetic effects during droplet heat-up.

5. Conclusions

The main objective with this work was to evaluate the performance of an industrial size PEHT-BLG reactor with respect to gas composition at different operational conditions. From the two experimental campaigns performed within this work the following conclusions can be drawn:

- The bulk composition of the product gas is mainly determined by the water gas CO-shift reaction and thus, by the operating temperature and j.
- Increased system pressure promotes H₂S in the gas.
- Increased j suppresses the amount of CH₄ in the gas.
- The amount of analyzed carbon containing gases increase with decreased black liquor flow rate to pressure ratio.
- At constant pressure, the heating value of the gas increase with increased black liquor flow rate to pressure ratio.
- Increased black liquor pre-heat temperature suppresses CH₄ and H₂S content in the gas.

Acknowledgements

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manuscript and discussions of the experimental results. Finally, the operators of the DP-1 from Chemrec KB, Smurfit Kappa Kraftliner AB, and SCA Packaging AB are especially acknowledged for invaluable assistance during the experiments.

References

Paper III

Wiunikka H., Carlsson P., Marklund M., Grönberg C., Pettersson E., Lidman M., Gebart R.,
Experimental investigation of an industrial scale black liquor gasifier. 2. The effect of quench
operation parameters on product gas composition. Submitted to Fuel
Experimental investigation of an industrial scale black liquor gasifier. Part 2. Influence of quench operation on product gas composition

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Abstract

Pressurised black liquor gasification combined either with a gas turbine or a catalytic fuel synthesis process is a novel technique for production of green electricity or second generation motor fuels. The composition of the gas produced in the gasifier may be important for the performance of either the gas turbine or the catalytic fuel synthesis process and different operating parameters of the gasifier may affect the composition of the produced gas. The aim with this study was to investigate the influence of some operating parameters on the final gas composition with special attention on the performance of the quench in the gasifier. The results show that system pressure, oxygen/black liquor flow rate ratio and the primary spray flow rate in the quench significantly affect the final gas composition. Furthermore, depending on the cooling rate in the quench, the hot reactor gas composition prior to the quench could either be preserved (high cooling rate) yielding the same final gas composition after the quench as in the hot reactor or shifted (low cooling rate) towards a higher concentration of H₂ and CO₂.

Keywords: gasification, black liquor, syngas composition, quench, water gas shift
1. Introduction

Chemrec AB:s technology for pressurised black liquor gasification combined with a catalytic process for synthetic motor fuel production has the potential to globally produce green motor fuels equivalent to over 45 billion liters/year of gasoline equivalent [1]. Black liquor is a byproduct of the chemical kraft pulping process and it consists of roughly 30% water, 30% inorganic cooking chemicals (valuable for the pulp mill) and 40% lignin and other organic substances separated from the wood during chemical pulping in a digester. To obtain a proof of the concept, a Development Plant (DP1) with a capacity of 20 ton dry solid of black liquor/24 h (~3 MWth) was commissioned in 2005. The gasifier is located next to the Smurfit Kappa Kraft-liner pulp and paper mill in Piteå, Sweden. The Chemrec DP1 is fully instrumented and is operated continuously by a 5-shift operating team to provide proof that the technology is sufficiently robust for industrial use and to provide valuable data for scale-up of the process. The plant has, as of October 2009, been operated for more than 11000 hours.

The main components of the black liquor gasifier are shown in Figure 1 [2]. The gasifier consists of a refractory lined oxygen blown entrained down-flow gasification reactor, with a centrally placed gas assisted burner that produces small black liquor droplets (~100 μm) by atomisation with oxygen followed by a direct quench. In the reactor, pressurised (30 bar) high temperature (~1050 ºC) gasification takes place, mainly through reactions between the black liquor and oxygen, steam and carbon dioxide producing a syngas (mainly H2, CO, H2O, CO2, CH4, and H2S) and a liquid smelt containing Na2CO3, Na2S and NaOH. The product gas and the smelt then enter a quench vessel beneath the reactor where rapid cooling occurs as the products are brought into direct contact with water droplets from several spray nozzles. The smelt droplets are separated from the gas flow and dissolved in a quench pool at the bottom of the gasifier to form green liquor. The saturated gas is thereafter cleaned from particles in a Counter Current Condenser (CCC) gas cooler. The dry (30 ºC) and almost particle free (30-100 μg/Nm³) syngas [3] is then analysed with conventional on-line gas instruments and finally combusted using a flare. In an industrial plant, the cooled syngas will go through an acid gas removal unit to remove the H2S and CO2 from the syngas. Thereafter, the H2/CO ratio will be adjusted in a CO-shift unit that precedes the catalytic conversion unit converting the syngas to high value fuels and chemicals.

The final composition of the syngas is important for the catalytic process design and different operating parameters of the gasifier are known to affect the composition of the product gas
that will form the final syngas. In an earlier paper by our group, an advanced gas sampling system was described that makes it possible to investigate the gas composition inside the current hot pressurised reactor [4]. In the first paper of this series, the gas sampling system was used to experimentally investigate the influence of process operation on the gas composition inside the hot reactor [5]. In that investigation it was found that the syngas composition in the hot reactor was affected by the system pressure, black liquor load, black liquor to oxygen mass flow ratio, and the black liquor temperature [5]. However, the composition of the syngas may also be influenced by chemical reactions and/or absorption when the raw product gas and smelt come in contact with the water spray and the green liquor pool in the quench. The aim with this second paper in the series is therefore to experimentally investigate the change in syngas composition as it flows through the quench and to investigate the influence from certain process parameters that change the operation of the quench.

The motivation for this investigation comes from an ambition to better understand the various stages in the current conversion process of black liquor and to provide experimental data that later on can be used to optimise the process and for validation of mathematical models (CFD models and thermo-chemical equilibrium models).

2. The quench

In general, gas from a gasification reactor is contaminated with various components that must be removed before the gas can be used in a synthesis process or for power production [6]. These contaminants, which may be particulates (soot or inorganic ash particles), sulphur or chlorine compounds and tars, must be removed from the gas. All such removal processes operate at a temperature considerably lower than that of the gasifier itself [6]. Therefore, the gas has to be cooled several hundred degrees.

One method often used to cool the gas during slagging gasification is to introduce fine water droplets into the hot gas and thus quench the conversion products by evaporation of the water. In contrast to ordinary gasification processes, the ash product from the current gasification concept (smelt dissolved in water forming green liquor in the quench) is an important by-product from the gasifier that must be recycled to the chemical pulping mill. Hence, proper operation of the quench in black liquor gasification is very important.
2.1. Geometry and function of the quench

The general principle of the quench in the current Chemrec type of gasifier was first proposed by Stigsson and Bernard [7] and a schematic sketch of their quench concept is presented in figure 2 [7]. In this paper a short description of the geometry and the function of the quench are given, adopted from the work by Stigsson and Bernard [7]. The hot product gas with smelt droplets from the reactor is forced to pass through the reactor throat and down into the downcoming quench tube. At the entrance of the quench tube, cooling liquid (water or condensate from the CCC) is injected into the gas flow through nozzles (primary spray). The gas is then cooled by evaporation of the primary spray to a predetermined temperature greater than the steam saturation temperature at the prevailing quench vessel pressure, to provide a gas containing superheated steam. The gas with its superheated steam is then forced to change direction and turn about 180° at the lower end of the downcoming quench tube. The gas then flows upwards and out of the outer surrounding tube concentrically arranged around the central downcoming tube.

The entrained particles, containing inorganic alkaline compounds, are forced by gravity and/or inertia to fall into the quench pool where the compounds are dissolved in water to form “green liquor”. The separated gas (with superheated steam) is then further cooled by a second cooling liquid (secondary spray) and finally bubbled through a water column before it leaves the quench vessel. The gas has now been cooled down to the steam saturation temperature at the prevailing quench vessel temperature. The level of the liquid in the quench pool is an operational parameter, which can be controlled by addition of cooling liquids and by withdrawal of green liquor.
2.2 Chemistry in the quench

The hot gas at the outlet of the reactor mainly consists of H2, CO, H2O, CO2, CH4, H2S, and COS [4, 5]. A typical gas composition (as dry and nitrogen free) before cooling is 34% CO2, 29% CO, 34% H2, 1.5% CH4, 1.5% H2S and 500 ppm COS. When the temperature in the top of the quench is reduced due to the evaporation of water from the primary spray, the composition of the gas may be changed either by the water gas shift reaction (R1), the hydrogenation reaction (R2) or the hydrolysis reaction (R3) [6]. The hydrogen reaction (R2) and the hydrolysis reaction (R3) control the relation between the H2S and COS.

\[
\text{CO(g)} + \text{H}_2\text{O(g)} \leftrightarrow \text{CO}_2(g) + \text{H}_2(g), -41 \text{ kJ/mol} \quad \text{(R1)}
\]

\[
\text{COS(g)} + \text{H}_2(g) \leftrightarrow \text{H}_2\text{S(g)} + \text{CO(g)}, +7 \text{ kJ/mol} \quad \text{(R2)}
\]

\[
\text{COS(g)} + \text{H}_2\text{O(g)} \leftrightarrow \text{H}_2\text{S(g)} + \text{CO}_2(g), -34 \text{ kJ/mol} \quad \text{(R3)}
\]

The smelt and the product gas also interact in the quench with water (in vapour or liquid phase) according to the following reactions (R4-R14). Reaction R4 describes the formation of Na2CO3 and H2S from Na2S, H2O and CO2. Reactions R5-R7 describe the solution of the smelt that consists of NaOH, Na2S, and Na2CO3 together with H2O producing a solution of Na+, OH−, HS−, and CO3²− ions (green liquor constitutes). Reaction R8 and R9 describe absorption of CO2 and H2S in the green liquor. Reactions R9-R12 describe the interaction of absorbed CO2 and H2S with the negative ions in the green liquor. Finally, reaction R13 and R14 describe the formation and destruction of HCO3−.

\[
\text{Na}_2\text{S(s)} + \text{H}_2\text{O(g)} + \text{CO}_2(g) \leftrightarrow \text{Na}_2\text{CO}_3(s) + \text{H}_2\text{S(g)}, -151 \text{ kJ/mol} \quad \text{(R4)}
\]

\[
\text{NaOH(s)} \leftrightarrow \text{Na}^+(aq) + \text{OH}^-(aq), -44 \text{ kJ/mol} \quad \text{(R5)}
\]

\[
\text{Na}_2\text{S(s)} + \text{H}_2\text{O(l)} \leftrightarrow 2\text{Na}^+(aq) + \text{HS}^-(aq) + \text{OH}^-(aq), -76 \text{ kJ/mol} \quad \text{(R6)}
\]

\[
\text{Na}_2\text{CO}_3(s) \leftrightarrow 2\text{Na}^+(aq) + \text{CO}_3^{2-}(aq), -26 \text{ kJ/mol} \quad \text{(R7)}
\]

\[
\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq), +20 \text{ kJ/mol} \quad \text{(R8)}
\]

\[
\text{H}_2\text{S(g)} \leftrightarrow \text{H}_2\text{S(aq)}, +19 \text{ kJ/mol} \quad \text{(R9)}
\]

\[
2\text{OH}^-(aq) + \text{CO}_2(aq) \leftrightarrow \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(aq), -157 \text{ kJ/mol} \quad \text{(R10)}
\]
As discussed by Stigsson and Bernard [7], when hot CO₂ containing gas is brought in contact with an alkaline solution such as green liquor, CO₂ tends to be absorbed into the solution and the resulting pH value of the green liquor is thereby lowered. If too much CO₂ is absorbed in the green liquor then HCO₃⁻ is formed according to reaction R13. This is, however, an undesirable compound in green liquor, since it increases the load on the causticizing system where sodium hydroxide is regenerated from the sodium carbonate in the green liquor. According to reaction R14, HCO₃⁻ and OH⁻ cannot co-exist in the green liquor at the same time. The formation of HCO₃⁻ in the green liquor can be minimised by cooling the hot gas in multiple stages in the quench and by separating the inorganic alkaline compounds from the hot gas at an intermediate temperature before the hot gas is cooled to the saturation temperature at the prevailing quench vessel pressure. Therefore, the gas is cooled by two different water sprays (primary and secondary) in the quench (see figure 2). The flow rates of these sprays can be controlled independently.

3. Experimental

3.1. Experimental campaigns

The influence of process parameters on the gas composition in the DP1 plant was investigated during two different measurement campaigns sufficiently separated in time to make them independent. The measurement campaigns were performed in May (8 different experiments) and October (44 different experiments) 2008. The experimental conditions of the gasifier during the May and October experimental campaigns are summarised in Table 1 and Table 2, respectively. During these measurement campaigns the influence from system pressure (relative), oxygen to black liquor flow rate ratio (O₂/BL), primary spray flow rate, black liquor temperature, and black liquor load (mass flow of black liquor) were investigated. In
addition, during the October campaign, the influence from secondary spray flow rate was also investigated.

The experimental DP1 black liquor gasifier is an industrial scale process and therefore the experiments performed in this work are not idealised. Instead they should be regarded as a benchmark for how the gas composition can be altered by changing the process conditions in the quench for a fully industrialised plant for black liquor gasification. Due to practical reasons, it is in most cases not possible to change only one parameter independently of the rest. For example, when the reactor pressure is increased it is desirable to maintain the same residence time of the gas in the gasifier and therefore the load (mass flow rates of black liquor and oxygen) is increased simultaneously. Furthermore, for safe long term operation of the gasifier, it is desirable to have the same process temperature (\(\sim 1050\) °C) in the reactor regardless of system pressure. The process temperature was measured with wall mounted ceramic insulated thermocouples. A lower process temperature may generate tar and soot in the gas that can cause deposits in downstream components and higher process temperature may reduce the life time of the refractory lining in the reactor. The requirement of constant reactor temperature will be satisfied by adjusting the black liquor to oxygen ratio when the system pressure is reduced. This is mainly to compensate for the larger relative heat loss from the hot reactor at lower loads. An example of the adjustment of oxygen equivalence ratio that is needed for the May and October campaigns can be seen in tables 1 and 2, respectively. In a separate set of experiments in both the May and October campaigns the process temperature was changed significantly (\(\pm 30\) °C) from \(\sim 1050\) °C. In this set of experiments the oxygen to black liquor mass flow ratio was varied with constant system pressure (30 bar May, 27 bar October). However, in order to ensure safe operation of the gasifier, the gasifier was only run for 1 hour at low or high oxygen to black liquor flow rate ratios (i.e. low and high process temperatures).

The experimental campaign in May was the first one performed with the high temperature gas sampling system installed and the experimental campaign in May was therefore not as well defined as in the October experimental campaign. For example, the primary spray flow rate was not constant when the system pressure and the oxygen equivalence ratio were varied. However, all relevant experimental data were recorded.
3.2. Experimental methods and experimental procedure

In order to determine the influence of quench operation on the raw product gas composition, gas samples were taken from two different positions in the plant simultaneously. The first position was inside the hot reactor near the outlet of the quench and the second position was immediately after the system pressure reduction valve, located after the CCC. The pressure at the second position was slightly above the atmospheric pressure while the pressure inside the gasifier varied between 15 and 30 bar. The raw gas composition at the outlet of the hot reactor was sampled with a high temperature gas sampling system, which has been thoroughly described elsewhere [4]. The high temperature gas sampling system quenched the sampled gas by rapid cooling via a large (choking) pressure drop at the probe tip and through contact with cold surfaces before it was collected in a pressure vessel. The vessel containing the gas sample was then removed from the sampling system and emptied into a Tedlar bag. The gas sample obtained after the pressure reduction valve was collected directly into a Tedlar bag. Both of the gas samples collected at the different positions were dry as the water vapour in the gas condenses when it is cooled. In the first case, when the gas was sampled with the high temperature sampling probe, the water was condensed inside the sampling system. In the second case, after the pressure reduction valve, the water had already been condensed in the CCC.

When the sampling procedure was finished, the operating condition of the gasifier was changed and allowed to stabilise at the new point of operation for at least 30 minutes before a new sample was taken. The gas samples in the two Tedlar bags were analysed with respect to CH₄, CO, CO₂, H₂, N₂, H₂S, COS, and O₂/Ar using a Varian CP-3800 gas chromatograph. In the results presented in this paper, the analysed concentrations of N₂ and O₂/Ar are not included and the sum of the other components has been normalised to dry and nitrogen free conditions. The analysed N₂ may originate from several sources in the process (e.g. atomisation media in the burner (59 kg/h), purging of the high temperature sampling probe, and mixing media in the green liquor pool) most of which will be negligible in a fully commercial process. A small part of the total analysed N₂ (together with O₂/Ar) can also come from air leakage in the handling procedure of the samples. From a process design point of view, the net gas composition, excluding inert N₂, is of most interest. Hence, all results in the paper are presented as dry nitrogen free.
During the experimental campaign in October, the gasifier was repeatedly operated at normal operating conditions (see the base case in table 2) to determine the stability and the repeatability of the measurements [4]. The standard deviation for the major gas components (CO₂, H₂, and CO) varies between 0.1-0.3 mole-%, 0.02-0.04 mole-% for H₂S and finally 5-22 ppm for COS [4]. It is therefore assumed in the parameter studies that only changes in gas composition larger than the maximum standard deviation for the base case are significant.

### 3.3. Black liquor composition

The black liquor used as fuel in the DP1 was delivered via an electrical heated pipe from the adjacent pulp and paper mill owned by Smurfit Kappa Kraftliner AB. The nominal mass flow rate of black liquor delivered to the DP1 (20 ton dry black liquor/24 h) corresponds to approximately 1 % of the total black liquor produced in the pulp and paper mill. The elemental compositions of the dry black liquor in the May and October campaigns are shown in table 3.

Compared to forest biomass [8] the black liquor consists of significantly more inorganic elements (originating from the cooking chemicals), especially Na, S, and K. The concentration of Cl is also significantly higher compared to forest biomass due to accumulation of Cl in the pulping process.

The black liquor composition during the experimental campaign in May consists of more C and H compared to the experimental campaign in October. This result in an increased calorific heating value (HHV), 13.37 MJ/kg in May compared to 12.57 MJ/kg in October. Furthermore, the sulphur content in the October campaign was slightly higher than in the May campaign.
4. Results

In this section, the influences of system pressure, O₂/BL flow rate ratio, primary spray flow rate, and secondary spray flow rate on the gas composition in the reactor and after the CCC are presented. Note that the CH₄ concentration in the gas samples is not discussed further in this paper since the CH₄ concentration have earlier been found to be unaffected when the product gas passes through the quench [4]. Furthermore, the influences of the considered process parameters on the CH₄ concentration have also been covered in the first paper in this series [5].

4.1. Effect of variations in system pressure

The effect of system pressure on the gas composition inside the reactor and after the CCC is presented in figure 3. When the system pressure was increased during the experimental campaigns in May and October, the concentrations of CO, H₂, H₂S and COS in the reactor increased and the concentration of CO₂ decreased. Since the relative increase in concentrations of both CO and H₂ are nearly the same in the reactor, the H₂/CO molar ratio inside the reactor was almost unaffected when the system pressure was increased.

When the system pressure was increased during the experimental campaign in May, the final concentrations of H₂ and H₂S after the CCC increased whereas the concentration of CO₂, CO, and COS decreased. Since the H₂ concentration increased and the CO concentration decreased, the H₂/CO molar ratio after the CCC also increased significantly when the system pressure was increased. Compared to the experimental campaign in May, the October campaign showed slightly different trends in the gas composition after the CCC when the system pressure was increased. Specifically, the concentration of CO increased instead of being reduced (as was found in the May campaign). However, for the other gas species after the CCC obtained in the October campaign, the same trends as in the experimental campaign in May could be found when the system pressure was increased. Since both the H₂ and CO concentrations in the gas increased when the system pressure was increased in the October campaign, the H₂/CO molar ratio was the same independent of the considered system pressures.

Figure 4 presents the relative change in product gas composition as it flows through the quench as a function of system pressure. A positive value for a specific gas component in figure 4 means that the concentration for that specific component is higher after the CCC than
in the reactor. Conversely, a negative value means that the concentration of the specific component after the CCC is lower than in the reactor.

During the experimental campaign in May, the concentrations of CO$_2$ and H$_2$ were higher and the concentration of CO was lower after the CCC compared to the conditions inside the reactor. The shift in concentrations of these gas components while passing the quench were enhanced by an increased system pressure. The resulting H$_2$/CO molar ratio was also higher after the quench than before the quench and this change in H$_2$/CO molar ratio increased with increasing system pressure. Furthermore, the H$_2$S concentration in the product gas increased when the gas flowed through the quench but the change in H$_2$S concentration appeared to be reduced when the system pressure was increased. The concentration of COS after the CCC was significantly lower than the concentration in the reactor and this reduction of COS in the gas was enhanced by an increased system pressure.

During the experimental campaign in October, the change in gas concentrations when the gas flowed through the quench was significantly lower compared to the experimental campaign in May. For system pressures above 15 bar in the October experimental campaign, the concentration of H$_2$ increased and the concentrations of CO$_2$ and CO decreased when the gas flowed through the quench. These changes in gas concentration were enhanced by an increased system pressure. For a system pressure of 15 bar, the concentrations of H$_2$ and CO were un affected by the quench. The change in concentration of CO$_2$ in the October campaign was opposite that observed in the May experimental campaign. Furthermore, the change in CO$_2$ concentration was practically unaffected by the system pressure. For system pressures above 15 bar, the H$_2$/CO molar ratio after the CCC was larger than in the reactor with an enhanced increase when the system pressure was increased. Furthermore, the H$_2$S concentration in the gas increased when the gas flowed through the quench. However, in contrast to the experimental campaign in May, the change in H$_2$S concentration appears have increased with increased system pressure. The concentration of COS after the CCC was significantly lower than the concentration in the reactor and the reduction of COS in the gas was enhanced by increased system pressure.
4.2. Influence of O₂/BL flow ratio

The influence of O₂/BL ratio on the gas composition in the reactor and after the CCC is presented in figure 5. Inside the reactor, when the O₂/BL ratio was increased during the experimental campaign in May, the CO concentration increased while the concentrations of H₂, H₂S, and COS decreased. However, the CO₂ concentration was practically unaffected by the O₂/BL ratio. Since the H₂ concentration decreased and the CO concentration increased, the resulting H₂/CO molar ratio in the reactor decreased when the O₂/BL ratio was increased. A slightly different behaviour for CO₂ and COS concentrations was discovered during the experimental campaign in October. The CO₂ concentration increased slightly and the COS concentration exhibited a non-linear behaviour when the O₂/BL ratio was increased. However, for the other gas components the trends were the same in both campaigns when the O₂/BL ratio was increased.

After the CCC, when the O₂/BL ratio was increased during the experimental campaign in May, the concentration of CO₂ increased slightly and the concentration of H₂S decreased. However, the concentrations of CO, H₂, COS and, hence, also the H₂/CO concentration ratio were practically unaffected by the O₂/BL ratio. During the experimental campaign in October, the concentrations of CO₂ and CO increased and the concentrations of H₂, H₂S, and COS along with the H₂/CO concentration ratio decreased when the O₂/BL ratio was increased.

The change in gas composition as it flows through the quench as a function of the O₂/BL flow ratio is presented in figure 6. During the experimental campaign in May, the concentrations of CO₂ and H₂ were higher and the concentration of CO was lower after the CCC compared to inside the reactor. Furthermore, this shift in concentrations was enhanced by an increasing O₂/BL ratio. The H₂/CO molar ratio was also higher after the quench and the change increased with increasing O₂/BL ratio. The H₂S concentration in the gas increased when the gas flowed through the quench but the change appears to be less at an increasing O₂/BL ratio. The concentration of COS after the CCC was significantly lower than in the reactor.

During the experimental campaign in October, the CO₂ concentration was slightly lower after the CCC compared to in the reactor. For a low O₂/BL ratio (0.267), the concentration of H₂ was slightly lower and the concentration of CO was slightly higher after the CCC compared to in the reactor. When the O₂/BL ratio increased, the H₂ and CO concentrations shifted so that more H₂ and less CO was found in the final syngas (after the CCC) compared to inside the reactor. Therefore, the change in H₂/CO molar ratio was negative at low O₂/BL ratios and
positive at high O2/BL ratios. As in the May experimental campaign, there was more H2S and less COS in the gas after the CCC compared to inside the reactor.

4.3. Primary spray
The influence of the primary spray flow rate on the gas composition is presented in figure 7. In the October experimental campaign, the influence of primary spray flow rate on the gas composition was investigated at three system pressures: 15, 20, and 27 bar while in the May experimental campaign the system pressure was 30 bar. The primary spray flow rate is unlikely to affect the gas composition in the reactor since the primary spray operates in the quench where the gas has left the reactor. Therefore, the small variations in the gas composition observed in the reactor, at the same reactor conditions, are most likely due to small uncontrolled process variations.

During the experimental campaign in October, a small increase in CO concentration and a small decrease in CO2 concentration in the final syngas composition after the CCC were measured when the primary spray flow rate was increased from 260 l/h to 540 l/h. This also led to a small decrease in the H2/CO molar ratio. The other gas components (H2, H2S and COS) were unaffected by the primary spray flow in the experimental campaign in May.

For a system pressure of 27 bar in the October experimental campaign, a small increase in CO concentration and a small decrease in CO2 concentration were measured after the CCC when the primary spray flow rate was increased from 350 to 1000 l/h. The H2/CO molar ratio was therefore also slightly reduced when the primary spray flow was increased. For system pressures of 20 and 15 bar, an increasing primary spray flow rate affected the concentrations of CO, CO2 and H2 in the same manner as for a system pressure of 27 bar. Considering the H2 concentration, it was either practically constant (at 20 bar) or increased slightly (at 15 bar) when the primary spray flow rate was increased. For all considered system pressures in the October experimental campaign, the COS concentration was observed to increase after the CCC when the primary spray flow rate was increased.

Figure 8 presents the relative change in gas composition as the gas flows through the system from the hot reactor and through the quench as a function of the primary spray flow rate. The gas concentrations of CO2 and H2 increased and the concentration of CO decreased from hot reactor to after the CCC in the experimental campaign in May. The shift in gas composition towards more CO2 and H2 and smaller amounts of CO was enhanced by a reduced primary spray flow rate. Consequently, the change in H2/CO molar ratio was also enhanced by
reducing the primary spray flow rate. The increase in H₂S concentration when the gas flowed through the quench was reduced and the reduction in COS concentration was enhanced by an increasing primary spray flow rate.

During the experimental campaign in October for system pressures 27 and 20 bar, the CO₂ and CO concentrations in the final gas after the CCC were lower and the H₂ concentration was higher. The change in CO₂ concentration caused by the quench was enhanced and the change in H₂ and CO was reduced by an increasing primary spray flow rate. The increase in H₂/CO molar ratio was reduced by an increasing primary spray flow rate. At 15 bar system pressure a slightly different behaviour of the H₂ and CO concentrations were found when the primary spray flow rate was increased. Higher concentrations of H₂ and CO were found in the final syngas, which is in contrast to the other considered system pressures during the same campaign where the change in gas composition of both H₂ and CO (increased) was enhanced by an increasing primary spray flow rate. Furthermore, the change in H₂/CO molar ratio was negative and this negative change was enhanced by an increasing primary spray flow rate.

Due to the relatively large variations in the reactor concentration of H₂S (see figure 7) between the different experiments, it is hard to determine the true influence of the primary spray flow rate on the change of H₂S concentration as the gas flows through the quench in the October experimental campaign. In general, the reduction in COS concentration when the gas flowed through the quench was decreased when the primary spray flow rate was increased.

4.4. Secondary spray
No significant effects on the final gas composition of CO₂, H₂, CO, H₂S and COS or the change in gas composition when it flows through the quench could be measured in this investigation when the secondary spray flow rate was reduced from 1500 l/h to 500 l/h.
5. Discussion

The focus on the current paper is on the function of the quench part in the DP-1 plant for black liquor gasification. Conditions inside the hot reactor and the influence from different process parameters on the reactor performance, are discussed in the first paper in this series [5].

5.1. Major gas components

The results presented above show that the relative amounts of the major components (CO₂, H₂, and CO) in the gas are affected as the gas flows through the quench. As an example, the H₂/CO molar ratio was in some cases found to be significantly higher after the CCC than in the reactor. This particular change in gas composition is believed to be caused mainly by interactions between water from the primary spray and the hot gas from the reactor. The change in gas composition from this was especially noticeable at a high system pressure. In the May experimental campaign the change in the major components was larger than in the October campaign. In both the May and October experimental campaign the load (flow of BL and oxygen) was increased when the pressure was raised. The flow rate of the primary spray was however the same independently of system pressure in the October campaign, 350, 700 or 1000 l/h. The main difference between the May and October experimental campaign was again that the load was significantly higher in the May campaign compared to the October campaign. In the same time, the primary spray flow rate was lower. Hence, it appears that the ratio between the primary spray flow rate and the load has a significant influence on the H₂/CO molar ratio in the cooled syngas.

In order to verify this hypothesis, the H₂/CO molar ratio in the reactor and after the CCC was plotted against the load in figure 10 for the experiments when the system pressure and the primary spray flow rate were varied. This data set was chosen since the reactor temperature was approximately the same (~1050 °C) in all of these experiments. For large primary spray flow rate/load ratios (kg/kg) the H₂/CO molar ratio in the reactor and after the CCC was almost the same (i.e. 1.2). However, when the primary spray flow rate/load ratio was reduced below ~ 0.6, the H₂/CO molar ratio after the CCC increased significantly compared to the H₂/CO molar ratio in the reactor. For a primary spray flow rate/load ratio as small as ~0.2 the H₂/CO molar ratio after the CCC is about 1.4.
In figure 11 the difference in gas composition between the CCC and the reactor is presented for the major gas components as a function of the primary spray flow rate/load ratio. Again, when this ratio was reduced below ~0.6, the concentration of H₂ and CO₂ in the resulting gas after the CCC increased and the concentration of CO decreased. This indicates that the primary spray flow rate has a significant effect on gas composition when the flow rate is below a certain value. For very low primary spray flow rate/load ratios (~0.2) the H₂ and CO₂ concentrations after the CCC have increased about 2%. For the same case the concentration of CO has been reduced about 4% units. An interesting observation for large primary spray flow rate/load ratios is that the CO₂ concentration after the CCC is lower than the CO₂ concentration in the reactor.

The apparent change of the major gas components as the gas flows through the quench are most likely explained by the water-gas shift reaction (R1). The partial pressure of water vapor in the gas increases in the quench due to extensive evaporation of water from the primary spray, which reduces the gas temperature. Both the increased partial pressure of water vapor and the reduced gas temperature shift the equilibrium gas concentration to more H₂ and CO₂ produced from CO and H₂O. For high primary spray flow rate/load ratios (> 0.6) the mass flow rate of water and the corresponding cooling rate for the gas is probably high enough to rapidly freeze the water-gas shift reaction and result in a gas composition after the quench that is almost the same as at the exit of the hot reactor. However, for low primary spray flow rate/load ratios (< 0.6) the temperature after the primary spray region is probably still sufficiently high and the cooling rate is sufficiently low to permit a shift in the gas composition towards more H₂ and CO₂ and lower amount of CO.

The observed reduction in CO₂ concentration when the gas flows through the quench for very large primary spray flow rate/load ratios may indicate that some CO₂ was absorbed by the green liquor or by smelt droplets in the quench. The temperature in the quench is reduced by the cooling water introduced via the primary spray and if enough water is introduced the syngas will be saturated with water vapour. Free (non evaporated) water droplets from the primary spray may then survive in the saturated gas above the green liquor surface, which may result in collisions with smelt droplets or with fume particles (formed from vaporisation and condensation of inorganic from the black liquor in the hot reactor) entrained in the gas flow, thus, forming small alkaline green liquor droplets (R5-R7). Acid CO₂ in the gas may thereafter be absorbed in these green liquor droplets (R8), which would lower the pH in the droplets. This would in its turn reduce the quality of the final green liquor (R9-R14). Thus, for
operating conditions resulting in a saturated gas, a further increase in primary spray flow rate/load ratio will increase the number of surviving water droplets in the gas results in an unwanted CO₂ absorption in the final green liquor.

The activity in the water gas shift reaction (R1) and the absorption of CO₂ in the green liquor are likely to be the main explanations for the influences of the different operating parameters on the gas composition that was observed in the experiments. A lower quenching rate at high system pressures (i.e. lower primary spray flow rate/load ratios) may explain why the shift towards higher concentrations of CO₂ and H₂ and lower concentrations of CO was stronger in the experimental campaign in May when the system pressure was increased, compared to the October campaign. This phenomenon also explains why the trend in CO concentration between the hot reactor and the final syngas was not the same when the system pressure was increased. In the October experimental campaign, the quenching of the water gas shift reaction in the primary spray region was much larger and the resulting final gas composition after the CCC was therefore almost the same as the gas composition in the reactor independent of the system pressure.

The quenching rate of the water gas shift reaction is also the most likely explanation for the shift by the quench towards more CO₂ and H₂ and smaller amount of CO was enhanced by an increased O₂/BL ratio in the experimental campaign in October. Since the temperature in the reactor increased with an increasing O₂/BL ratio, the quenching rate from the primary spray (at similar flow rates) was lower. Hence, a stronger shift in gas composition occurred.

As discussed above, an increased primary spray flow rate at constant system pressure leads to a higher quenching rate of the water gas shift reaction and less or no change in gas composition as it passes through the quench. The reduction in CO₂ concentration caused by the quench in the October experimental campaign may be a combination of a relatively high quenching rate in the primary spray region and a possible absorption of CO₂ in the droplets originating from the primary spray. The final concentration of CO₂ in the syngas after the quench is therefore the result of a balance between these two mechanisms. At low primary spray flow rates, the water gas shift reaction has the possibility to become significant. This is supported by the observation that there was a positive change in H₂ concentration and negative change in CO₂ concentration when the gas flowed through the quench. The expected positive change in CO₂ concentration (from the water gas shift reaction) is counteracted by the absorption of CO₂ in the droplets from the primary spray, leading to a small negative
change in CO₂ concentration. When the primary spray flow rate is increased the water gas shift reaction is becoming increasingly inactive, leading to almost no change in H₂ and CO concentrations through the quench. Simultaneously, the absorption of CO₂ in the water droplets increases, leading to a higher negative change of CO₂ when the primary spray flow rate is increased. Furthermore, at sufficiently high primary spray flow rates, compared to the flow of syngas, the absorption of CO₂ in the droplets is so high that it significantly affects the final gas composition with respect to H₂ and CO. Therefore, both the H₂ and CO concentrations are higher in the final gas compared to inside the reactor.

5.2. Minor gas components (H₂S and COS)

The effects of system pressure and O₂/BL ratio on the concentrations of H₂S and COS in the gas have been discussed by Carlsson et al. [5]. The experimental results in this paper indicate that the concentration of H₂S after the CCC is higher than the concentration in the reactor. This indicates that sulphur was released to the gas phase from the smelt droplets or fume particles suspended in the gas and/or from the green liquor pool. One possible explanation based on reaction (R4), is that H₂S can be released to the gas phase when Na₂S (as smelt droplets or fume particles) reacts with H₂O and CO₂ in the gas producing Na₂CO₃ and H₂S in the primary quench zone. Furthermore, dependent on the pH (amount of absorbed CO₂) in the green liquor, the acid H₂S can either be absorbed or released to the gas phase (R7).

In order to investigate if the primary spray flow rate/load ratio has an effect on the H₂S and COS concentrations when the gas flows through the quench, the differences in H₂S and COS concentrations between the CCC and the reactor are presented in figure 12 (same experiments as in figure 10 and 11). The results shown in figure 12 indicate that the increase in H₂S concentration also is dependent on the primary spray flow rate/load ratio since the increase in H₂S concentration was generally higher at low primary spray flow rate/load ratios. Therefore, it is possible that reaction R4 also is quenched by a high primary spray flow rate/load ratio in a similar manner as in the case of the water gas shift reaction.

In general, the relative reduction of the COS concentration is significant when the gas flowed through the quench. The reduction of COS is probably a result of the hydrolysis reaction (R3), in which COS react with H₂O to produce H₂S and CO₂. Hydrolysis of COS in the quench has earlier been observed during pressurised black liquor gasification [9]. The production of H₂S from COS can however not explain the total increase in H₂S concentration since the concentration of COS is small relative to H₂S. Furthermore, no correlation between the
primary spray flow rate/load ratio on the change in COS concentration between the CCC and the reactor was found (see figure 12).

The concentrations of H₂S and COS in the gas (both from the reactor and after the CCC) were significantly higher in the October campaign compared to the May campaign. The increase in the gaseous sulphur components is most likely a result of the higher sulphur content (~10 %) in the black liquor used in the October campaign compared to the May campaign (see table 3).

5.3. Optimal operation of the gasifier
As mentioned above, the resulting gas from black liquor gasification can either be used for power production or in a synthetic fuel production process. Important parameters that reflect the quality of the syngas are presented in table 4. In the case of power production, the gas will be burned in a gas turbine located downstream the CCC. An important parameter in this case is the heating value of the gas (LHVPower). A gas with higher LHVPower burns more easily in the gas turbine. Furthermore, it also give an indication of the efficiency of the gasifier itself since more energy is stored in the produced gas for a gas with higher LHVPower and that energy (chemical bound) is transformed into mechanical work when the gas is burned in the gas turbine. If the mass flow of produced gas is approximately the same between two cases. The case with highest LHVPower also has the highest efficiency of the gasifier and the gas turbine. To get the correct picture one need to know the total mass flow of produced gas together with the LHVPower so that the energy balance of the gasifier can be calculated. However, since the mass flow of produced gas is unknown, we are limited to use LHVPower instead of the total energy flow as an indicator for optimal operation of the gasifier. The CH₄ concentration in the gas may be important since it gives an indirect indication of the tar content in the gas leaving the hot reactor. Most of the tars condense in the quench and the CCC and if the tar concentration is too high, operational problems of the plant may occur due to accumulation of the tars in the system.

From a power production point of view, it is positive to increase the system pressure from 15 bar up to about 30 bar since the LHVPower increases significant (~9 %) and the relatively small increase in CH₄ concentration is probably not a problem. The drawback by increasing the system pressure is that the H₂S concentration in the gas increases with increasing system pressure (see figure 3). This has two negative side effects: since more of the S in the black liquor will go to the gas phase the concentration of HS⁻ (active cooking chemical) in the green liquor will be reduced. Secondly, the H₂S in the gas will be converted into SO₂ in the
combustion process in the gas turbine and therefore the emissions of SO₂ increases with increasing system pressure. The LHV_{power} was significantly reduced by an increased O₂/BL flow ratio, which was mainly due to significantly lower CH₄ concentrations in the gas. The reactor should therefore be operated at the lowest possible O₂/BL flow ratio without producing too much tar (indicated by the CH₄ concentration). Furthermore, it is desirable to freeze the water gas shift reaction in the primary quench zone, since it is exothermic (see R1). Otherwise, as observed during the May experimental campaign the LHV_{power} of the gas decreased slightly when it flowed through the quench. If the primary spray flow rate is sufficiently large (October experimental campaign), the LHV_{power} of the gas after the CCC can become higher since inert CO₂ is absorbed in the green liquor, which in turn negatively affects the quality of the green liquor. To optimise the process for power production, the primary spray flow rate should be held at a level high enough to freeze the water gas shift reaction but not higher in order to avoid undesirable absorption of CO₂ in the green liquor.

Compared to power production, the issues connected to optimal gas composition for the production of synthetic fuels are more complicated and dependent on the fuel to be synthesized (the chemical structure differ) and the applied synthesis technique. Still, the heating value of the resulting gas is highly important considering the efficiency of the gasification process. However, in this case the concentrations of CH₄ and H₂S can be regarded as inert species regarding the heating value of the gas since the production of synthetic fuels is based on different combinations of H₂ and CO. Therefore, the useful heating values for synthetic fuel production (LHV_{fuel}), where CH₄ and H₂S are regarded as inert species in the synthesis process (0 in heating value), are presented in table 4. Another important parameter considering fuel synthesis is the H₂/CO molar ratio. Depending on the final fuel, the fuel synthesis method and company specific details the optimal H₂/CO molar ratio may vary. In general, an optimal H₂/CO molar ratio for methanol production is between 3 to 5 in gas phase reactors whereas in liquid phase reactors a lower H₂/CO molar ratio is used, typically 1 to 2 [10]. The methanol can thereafter be used as feedstock for production of other motor fuels such as synthetic gasoline or dimethyl ether (DME) [11, 12].

The CH₄ and H₂S contributions to the total heating value were significant since the LHV_{fuel} (see table 4) was 8-21% lower than the LHV_{power} dependent on the operational condition of the gasifier. Similar to the power production case, from a fuel synthesis point of view it is positive to increase the system pressure from 15 bar to about 30 bar since the LHV_{fuel} significantly increases (~8%). Furthermore, the H₂/CO molar ratio also increased when the
system pressure was increased. This may be positive or negative, dependent on the configuration of the downstream fuel synthesis process (optimal H₂/CO molar ratio: 1 - 2). The drawback with increasing system pressure is that the H₂S concentration in the gas increases (see figure 3) and, as mentioned earlier in the paper, it reduces the concentration of HS⁻ in the green liquor. Furthermore, since H₂S deactivates the catalyst, the demands on the acid gas removal unit increase with increasing system pressure. In contrast to power production and LVH_{power}, the LHVFuel was not practically affected by the O₂/BL flow ratio. If the water-gas shift reaction is quickly quenched in the primary quench zone, the H₂/CO molar ratio will decrease when the O₂/BL ratio is increased and, again, dependent on the downstream fuel synthesis process this can be positive or negative. However, if the water-gas shift is not prevented, the H₂/CO molar ratio can be the same independent of the O₂/BL ratio. The positive thing with an increasing O₂/BL ratio is then that the tar content in the syngas can be reduced (indicated by a reduced CH₄ concentration) without reducing the LHVFuel or the H₂/CO molar ratio in the gas. Another positive side effect with an increasing O₂/BL ratio is that the H₂S concentration in the gas is reduced (see figure 5) with an increased O₂/BL ratio and thereby the acid gas removal needs of the gas are also reduced. The drawback is that the temperature in the hot reactor will increase and this can negatively affect the life time of the refractory lining surrounding the hot reactor.
6. Conclusions

In this paper, the influence of system pressure, O$_2$/BL ratio, primary and secondary spray flow rates on the composition of the gas (both in the reactor and after the CCC) during pressurised black liquor gasification was investigated experimentally. The following conclusions about the major gas components (CO$_2$, CO, and H$_2$) could be drawn from the results presented in this paper:

- The system pressure, O$_2$/BL flow ratio, and the primary spray flow affect the final gas composition of CO$_2$, CO, and H$_2$ after the quench. The system pressure and O$_2$/BL flow ratio also affect the concentrations of CO$_2$, CO and H$_2$ inside the hot reactor.

- The primary spray flow rate/load (mass flow of black liquor and oxygen) ratio has a critical value of about 0.6 below which concentrations of CO$_2$, CO, and H$_2$, are significantly changed in the quench.

- For high primary spray flow rate/load ratios, chemical reactions in the quench are freeze and therefore the gas concentration after the quench is nearly the same as in the hot reactor.

- For low primary spray flow rate/load ratios, the chemistry in the quench is highly influenced by the water-gas shift reaction and the gas composition after the quench is shifted to more H$_2$ and CO$_2$ and a smaller amount of CO than in the hot reactor.

- For high primary flow rates, CO$_2$ absorption can become significant.

The following conclusions can be drawn about the minor gas components (H$_2$S and COS):

- The concentration of H$_2$S increases both in the reactor and after the CCC when the system pressure is raised.

- The concentration of COS increases in the reactor but generally not after the CCC when the system pressure is raised.

- The concentration of H$_2$S (both in the reactor and after the CCC) is reduced when the O$_2$/BL ratio is increased.
• The concentrations of both H₂S and COS are significantly changed when the gas flows through the quench. The concentration of H₂S after the CCC increases while the concentration of COS is reduced compared to inside the reactor.

• The increase in H₂S after the quench cannot be explained only by the hydrolysis of COS. A likely additional mechanism is release of H₂S from smelt droplets or fume particles in the primary quench zone and/or from the green liquor pool.
Acknowledgement

The authors of this paper would like to thank the Swedish Energy Agency, Mistra, Smurfit Kappa Kraftliner AB, SCA Packaging AB, Södra Cell AB, Sveaskog AB, Chemrec AB, and the County Administrative Board of Norrbotten for funding this work through the BLG II research program. The authors especially would like to thank Chemrec KB for letting us conduct experiments in the DP1 and publish the results from those experiments. Peter Sikström, Johan Löfström and Fredrik Granberg, at Chemrec KB are acknowledged for helping us with the planning of the experimental campaigns in the DP1. Mats Lindblom and Ragnar Tegman, at Chemrec AB, are acknowledged for helpful comments on the manuscript and discussions of the experimental results. Finally, the operators of the DP1 from Chemrec KB, Smurfit Kappa Kraftliner AB, and SCA Packaging AB are especially acknowledged for invaluable assistance during the experiments.
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Tables

Table 1. Operation condition of the gasifier during the May campaign and where the results appears in the paper (figure number). The main operating parameters of interest (for example the pressure) appears in the heading and in bold text in the table. If another operating parameter is constant (for example the O2 temperature when pressure was varied) it appears once in the table under the pressure heading. If other operating parameters also change when the main parameter is changed the actual value for each parameter value appears in the table (for example BL flow when the pressure was varied).

<table>
<thead>
<tr>
<th>Main parameter</th>
<th>Base case</th>
<th>Pressure (15 → 30)</th>
<th>O2/BL ratio (0.285 → 0.313)</th>
<th>Prim. Spray (260 → 540)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Other parameters</td>
<td>30</td>
<td>15 20 25 30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Pressure [bar]</td>
<td>1250</td>
<td>625 830 1039 1252</td>
<td>1250 1250 1220</td>
<td>1250</td>
</tr>
<tr>
<td>BL flow rate [kg/h]</td>
<td>145</td>
<td>130 132 133 142</td>
<td>145</td>
<td>145</td>
</tr>
<tr>
<td>BL temp. [ºC]</td>
<td>375</td>
<td>203 260 320 375</td>
<td>356 375 383</td>
<td>375</td>
</tr>
<tr>
<td>O2 flow rate [kg/h]</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>20</td>
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<tr>
<td>O2 temp. [ºC]</td>
<td>260</td>
<td>430 530 630 730</td>
<td>150 260 130</td>
<td>260 540</td>
</tr>
<tr>
<td>Prim. spray flow rate [l/h]</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>Sec. spray flow rate [l/h]</td>
<td>3</td>
<td>5</td>
<td>7</td>
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</tr>
</tbody>
</table>
Table 2. Operation condition of the gasifier during the October campaign.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Base case</th>
<th>Pressure (15 → 27)</th>
<th>O₂/BL ratio (0.267 → 0.305)</th>
<th>Prim. Spray (350 → 1000)</th>
<th>Sec. spray (500 → 1500)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>27</td>
<td>15 20 27</td>
<td>15 15 15 20 20</td>
<td>27 27 27 27 27</td>
<td>27</td>
</tr>
<tr>
<td>BL flow rate (kg/h)</td>
<td>870</td>
<td>465 645 870</td>
<td>485 485 485 645 645</td>
<td>870 870 870 870 870</td>
<td>870</td>
</tr>
<tr>
<td>BL temp. (°C)</td>
<td>140</td>
<td>140 140 140</td>
<td>140</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>O₂ flow rate (kg/h)</td>
<td>254</td>
<td>147 192 234</td>
<td>232 254 266</td>
<td>147 147 192 192</td>
<td>254</td>
</tr>
<tr>
<td>O₂ temp. (°C)</td>
<td>50</td>
<td>50 50 50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Prim. spray flow rate (l/h)</td>
<td>700</td>
<td>700 700 700</td>
<td>350 700 1000 350 700 1000</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>Sec. spray flow rate (l/h)</td>
<td>1500</td>
<td>1500 1500 1500</td>
<td>1500</td>
<td>1500</td>
<td>1500</td>
</tr>
<tr>
<td>Figure</td>
<td>3</td>
<td>5 7</td>
<td>9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3. Chemical analysis for the black liquor for the May and October campaign. DS (Dry Solid), HHV (Calorific Heating Value).

<table>
<thead>
<tr>
<th></th>
<th>May</th>
<th>October</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS</td>
<td>72.4</td>
<td>75.2</td>
<td>wt-%</td>
</tr>
<tr>
<td>C</td>
<td>33.8</td>
<td>31.3</td>
<td>wt-% dry</td>
</tr>
<tr>
<td>H</td>
<td>3.6</td>
<td>3.4</td>
<td>wt-% dry</td>
</tr>
<tr>
<td>O</td>
<td>35.1</td>
<td>37.3</td>
<td>wt-% dry</td>
</tr>
<tr>
<td>N</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>wt-% dry</td>
</tr>
<tr>
<td>S</td>
<td>5.1</td>
<td>5.6</td>
<td>wt-% dry</td>
</tr>
<tr>
<td>Na</td>
<td>20.2</td>
<td>20.1</td>
<td>wt-% dry</td>
</tr>
<tr>
<td>K</td>
<td>2.2</td>
<td>2.3</td>
<td>wt-% dry</td>
</tr>
<tr>
<td>HHV</td>
<td>13.37</td>
<td>12.58</td>
<td>MJ/kg dry</td>
</tr>
</tbody>
</table>
Table 4. Important parameters in the syngas for power or synthetic fuel production during the experimental campaign in May and October.

<table>
<thead>
<tr>
<th></th>
<th>May</th>
<th>October</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pressure</td>
<td>O₂/BL</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>CH₄ (%)</td>
<td>1.48</td>
<td>1.56</td>
</tr>
<tr>
<td>LHVₚₒᵣᵦ (MJ/kg)</td>
<td>7.32</td>
<td>7.91</td>
</tr>
<tr>
<td>ΔLHVₚₒᵣᵦ (MJ/kg)</td>
<td>0.01</td>
<td>-0.18</td>
</tr>
<tr>
<td>LHVₚₑᵦ (MJ/kg)</td>
<td>6.63</td>
<td>7.11</td>
</tr>
<tr>
<td>ΔLHVₚₑᵦ (MJ/kg)</td>
<td>-0.06</td>
<td>-0.20</td>
</tr>
<tr>
<td>H₂/O</td>
<td>1.25</td>
<td>1.39</td>
</tr>
<tr>
<td>Δ(H₂/O)</td>
<td>0.11</td>
<td>0.23</td>
</tr>
</tbody>
</table>

LHVₚₒᵦ = LHVₚₒᵦ after the CCC - LHVₚₒᵦ in the reactor.

LHVₚₑᵦ = LHVₚₑᵦ after the CCC - LHVₚₑᵦ in the reactor.

H₂/O = H₂/O after the CCC - H₂/O in the reactor.
Figure captions

Fig. 1. Schematic drawing of the PEHT-BLG process [2].

Fig. 2. Schematic drawing of the quench from [7]. (1) reactor, (2) throat, (3) downcoming tube, (4) primary spray (5) smelt separation region, (6) upcoming tube, (7) secondary spray, (8) gas outlet, (9) green liquor pool, and (10) green liquor outlet.

Fig. 3. Influence of system pressure on the gas composition.

Fig. 4. Influence of system pressure on the change in gas composition when it flows through the quench.

Fig. 5. Influence of O₂/BL ratio on the gas composition.

Fig. 6. Influence of O₂/BL ratio on the change in gas composition when it flows through the quench.

Fig. 7. Influence of primary spray flow rate on the gas composition.

Fig. 8. Influence of primary spray flow rate ratio on the change in gas composition when it flows through the quench.

Fig. 9. H₂/CO ratio as a function of the primary spray flow rate divided with load (BL and O₂ flow rate) of the gasifier.

Fig. 10. Influence from primary spray flow rate to load ratio on the change in major gas composition (CO₂, H₂ and CO) when the gas flows from the hot reactor through the quench. The different symbols represent differences in concentrations (e.g. CO₂ CCC – CO₂ reactor).

Fig. 11. Influence from primary spray flow rate to load ratio on the change in minor gas composition (H₂S and COS) when the gas flows from the hot reactor through the quench. The different symbols represent differences in concentrations (e.g. CO₂ CCC – CO₂ reactor).
Fig. 2.
May

October

Fig. 3.
Fig. 4.
Fig. 5.
<table>
<thead>
<tr>
<th>May</th>
<th>October</th>
</tr>
</thead>
<tbody>
<tr>
<td>![Graph May]</td>
<td>![Graph October]</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>![Legend] CO₂</td>
<td>![Legend] CO₂</td>
</tr>
<tr>
<td>![Legend] H₂</td>
<td>![Legend] H₂</td>
</tr>
<tr>
<td>![Legend] H₂S</td>
<td>![Legend] H₂S</td>
</tr>
</tbody>
</table>

Fig. 6.
Fig. 7.
May (30 bar)

October (27 bar)

October (20 bar)

October (15 bar)

Fig. 8.
Fig. 9.
Fig. 11.
Paper IV

Experiments and mathematical models of black liquor gasification – influence of minor gas components on temperature, gas composition, and fixed carbon conversion

PER CARLSSON, MAGNUS MARKLUND, ERIK FURUSJÖ, HENRIK WIINIKKA, and RIKARD GEBART

ABSTRACT: In this work, predictions from a reacting Computational Fluid Dynamics (CFD) model of a gasification reactor are compared to experimentally obtained data from an industrial pressurized black liquor gasification plant. The data consists of gas samples taken from the hot part of the gasification reactor using a water cooled sampling probe. During the considered experimental campaign, the oxygen-to-black liquor equivalence ratio ($\lambda$) was varied in three increments, which resulted in a change in reactor temperature and gas composition. The presented numerical study consists of CFD and thermodynamic equilibrium calculations in the considered $\lambda$-range using boundary conditions obtained from the experimental campaign. Specifically, the influence of methane concentration on the gas composition is evaluated using both CFD and thermodynamic equilibrium. The results show that the main gas components (H$_2$, CO, CO$_2$) can be predicted within a relative error of 5% using CFD if the modeled release of H$_2$S and CH$_4$ are specified a priori. In addition, the calculations also show that the methane concentration has large influence on the reactor outlet temperature and final carbon conversion.

Application: This work shows how predictions from a CFD model compare to experimental data and thermodynamic equilibrium calculations. By comparing predictions from the mathematical models with experimental data and developing the models, a deeper understanding of a complex process can be achieved. If properly validated, the mathematical models can then be used in optimization and scale up of entrained flow gasifiers.
GASIFICATION

was varied in three increments affecting the temperature and gas composition inside the reactor.

The aim of the present work was to assess the performance of an updated version of a previously developed CFD reactor model [4] and to identify possible modifications to improve the model predictions. Special emphasis is put on the influence of methane concentration on local gas composition. Furthermore, to aid in the evaluation of the CFD model predictions, thermodynamic equilibrium calculations were performed using the commercially available thermodynamic equilibrium and phase diagram software FactSage [5] and an in-house thermodynamic equilibrium code developed by Furusjö (a co-author of this paper).

EXPERIMENTAL

Gas samples were withdrawn from the hot part of the DP-1 gasification reactor using a water-cooled gas sampling probe specially designed to quench the gas and, thereby, to freeze any possible chemical reactions when the gas flows through the probe [2]. The gas samples were collected approximately 0.6 m above the outlet of the DP-1 gasification reactor (see position in Fig. 2).

The collected gas samples were analyzed with respect to CH₄, CO, CO₂, H₂, N₂, H₂S, COS, and O₂/Ar using a Varian CP-3800 gas chromatograph. During the experimental campaign, which took place in October of 2008, several operating parameters were varied [3] and in the present work the obtained results from the variations in oxygen-to-black liquor equivalence ratio (defined as \( \lambda = (x_{O_2} - x_{fuel}) / (x_{O_2,stoich} - x_{fuel,stoich}) \), where \( x \) is mol fraction) were used to evaluate the performance of the CFD reactor model. The experimental data consist of gas compositions for three different equivalence ratios. Table I summarizes the main operational parameters in the experiments.

Table I. Operating parameters for the DP-1 gasifier during the experimental campaign.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Case 1</th>
<th>Case 2</th>
<th>Case 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>bar(g)</td>
<td>27</td>
<td>27</td>
<td>27</td>
</tr>
<tr>
<td>Black liquor mass flow rate</td>
<td>kg/h</td>
<td>870</td>
<td>870</td>
<td>870</td>
</tr>
<tr>
<td>Black liquor pre-heat</td>
<td>°C</td>
<td>140</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>O₂ mass flow rate</td>
<td>kg/h</td>
<td>235</td>
<td>254</td>
<td>265</td>
</tr>
<tr>
<td>N₂ mass flow rate</td>
<td>kg/h</td>
<td>47</td>
<td>47</td>
<td>47</td>
</tr>
<tr>
<td>O₂ / BL</td>
<td></td>
<td>0.270</td>
<td>0.292</td>
<td>0.305</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>-</td>
<td>0.403</td>
<td>0.435</td>
<td>0.454</td>
</tr>
</tbody>
</table>

As Table I shows, only the oxygen mass flow rate was used to get a corresponding change in oxygen to black liquor mass flow rate ratio and consequently to the oxygen-to-black liquor equivalence ratio during the experimental campaign. The experimentally obtained results are described and evaluated in Carlsson et al. [3] but are reproduced here in Fig. 3 for the sake of clarity.

MATHEMATICAL MODELING

In the current work, CFD was used as a tool to predict gas composition and temperature distribution inside the DP-1 gasification reactor. To further aid in the evaluation of the results, additional thermodynamic equilibrium calculations were performed. The following subsections contain general descriptions of the CFD model and the thermodynamic equilibrium code, as well as the implemented boundary conditions used to predict the influence of \( \lambda \) on the local gas composition.

CFD model

The DP-1 reactor is an axi-symmetric entrained-flow reactor with the spray burner centrally placed at the reactor top (Fig. 1). The reactor internal dimensions are 2.3 m in height and 0.6 m in inner diameter. Based on the rotational symmetry, the reactor geometry was modeled as a 2D slice using periodic azimuthal boundary conditions. Regarding the wall boundary, estimates have shown that the heat loss in the plant through the reactor wall is approximately 90 kW or about 3% of the total thermal throughput at full capacity. Based on this, heat losses through the modeled refractory lined reactor wall were specified using a uniformly distrib-
uted heat loss along the wall. The burner was modeled as a simplified spray burner with concentric annular inlets where oxygen and discrete black liquor droplets enter the gasifier at a prescribed range of angles and velocities. The two-phase flow consisting of dispersed black liquor particles and gases was modeled using the Euler – Lagrange formulation. In the present paper, the black liquor spray was represented by 1003 discrete particles having a fitted Rosin Rammler distribution of power 2 and size 200 μm. The droplet size distribution and flow velocity are consistent with data from nozzle experiments measured by phase Doppler anemometry.

To model turbulence, the k-ε model with scalable wall functions was used. To include effects of turbulence on the discrete particles, a turbulent dispersion model was introduced as suggested by Gosman and Ioannides. The radiative heat transfer was modeled using the Discrete Transfer radiation model by Lockwood and Shah, treating the wall as optically smooth with a radiative emissivity of 0.5. The absorption coefficient for the gas was calculated as the mass weight average of the participating species.

In the present paper, the simplified gas phase reaction scheme by Jones and Lindstedt, as concerns Reactions (1-3) and (5), together with CO oxidation (Reaction (4)) was implemented as done by others. Regarding the sulfur chemistry in the gas phase, H2S (released during pyrolysis) was treated as inert.

Char gasification and smelt formation reactions were modeled as Reactions (6-8) below belusing the reaction mechanisms and coefficients as described by Marklund.

\[
\begin{align*}
\text{CH}_4 + \frac{1}{2}\text{O}_2 & \rightarrow \text{CO} + 2\text{H}_2 \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \\
\text{H}_2 + \frac{1}{2}\text{O}_2 & \rightarrow \text{H}_2\text{O} \\
\text{CO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CO}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \\
\text{C} + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 \\
\text{C} + \text{CO}_2 & \rightarrow 2\text{CO} \\
\text{C} + \frac{1}{2}\text{Na}_2\text{SO}_4 & \rightarrow \frac{1}{2}\text{Na}_2\text{S} + \text{CO}_2.
\end{align*}
\]

The model was implemented in the commercial CFD software package Ansys CFX where drying and pyrolysis were treated in a similar manner as char gasification and smelt formation through multiphase reactions implemented in user defined FORTRAN subroutines.

**Material description**

In the CFD model, the materials have to be described as specified species. Hence, the elemental or ultimate analysis needed to be transformed into the considered species. Based on the detailed elemental composition in Table II, the ultimate analysis was simplified by lumping K together with Na and neglecting the small amounts of Cl and N, thus forming a simplified elemental composition of the modeled black liquor (Table II).

By converting from mass to mole fractions, the simplified ultimate analysis was written as a row vector \(\mathbf{ev}\) where \(\mathbf{ev}(j)\) is the molar fraction of element \(j\). The different species were then described by a matrix \(\mathbf{S}\), defined as follows in Eq. (1):

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2
\]
Where $m$ is the number of considered species that should be present in the CFD model and $n$ is the number of elements in the element vector. The matrix elements ($S_{ij}$) describe how many moles of element $j$ it takes to construct one mol of species $S_i$. From the species matrix ($S$) and the element vector ($ev$), a system of linear equations (Eq. (2)) was formulated:

$$S^T p = e_i$$  \hspace{1cm} (2)

Where $p(i)$ is the mol fraction for each respective species. Since the number of model species was greater than the number of elements, the system is underdetermined; that is, the number of unknowns ($p$) was greater than the number of formulated equations ($-e_i$). To resolve this, a constraint matrix ($C$) and a constraint vector ($cv$) were defined and a similar system as in Eq. (1) was formulated. The matrix elements of $C$ and the constraint vector ($cv$) were used to define ratios between the different species, as in Eq. (3):

$$C^T p = cv$$  \hspace{1cm} (3)

In order to solve the system of equations and obtain the composition of the different species in the black liquor, the following constraints were used (as in [4]):

- Half of the carbon was modeled as fixed, i.e., char.
- The molar ratio between CO and CO$_2$ was equal to unity in the pyrolysis step.
- The molar ratio Na$_2$SO$_4$ over Na$_2$S was 8.
- The molar concentration of NaOH in dry black liquor was specified to 0.50%.
- All water is evaporated during drying.

Currently, the CFD model does not contain a detailed reaction mechanism for H$_2$S. Thus, the amount of H$_2$S released during pyrolysis will not react in the gas phase or with the smelt in the black liquor particles. However, as can be seen in Fig. 3, the H$_2$S concentration varies with the oxygen-to-black liquor mass flow rate ratio. To take this into consideration, different amounts of H$_2$S were released during pyrolysis as a function of the oxygen-to-black liquor equivalence ratio. Furthermore, previous calculations [4] have shown that the CFD model is unable to predict the CH$_4$ concentration at the outlet of the gasifier. To investigate the influence of this, part of the CH$_4$ released during pyrolysis was modeled as inert in a similar manner as with H$_2$S. Table III summarizes the constraints on H$_2$S and CH$_4$.

Table IV presents the material composition obtained from this solution method. As can be seen in this table, there
is a small difference in the experimentally obtained heating value (Table II) and the modeled heating values. To ensure consistency between the experimental results and the model, pyrolysis was treated as a multiphase reaction, with the heat of reaction chosen so that the modeled and experimental heating value became equal.

Thermodynamic equilibrium model
The thermodynamic equilibrium simulations used in this paper were carried out using FactSage [5] and SIMGAS, which is an in-house gasification simulation tool. Details regarding FactSage are covered extensively in the literature and will not be explained here.

SIMGAS is implemented in the Matlab platform and based on system Gibbs energy minimization under the assumption of ideal mixtures. The tool uses an active-set method [16] to solve the constrained non-linear minimization problem with the chemical composition of gas and smelt phases as independent variables. To obtain a good starting point for the non-linear optimization loop, an approximate linear problem is solved at first. The element balances are implemented as linear constraints.

The approach uses a set of chemical components that are postulated to be present in the equilibrium mixture. The quantitative composition of the mixture is then calculated by the minimization algorithm, based on thermodynamic data of the components and element balances. This may result in a mixture composition where some of the postulated components are not present; i.e., the calculated concentration is zero but the algorithm cannot "suggest" new components, so it is of utmost importance to specify a relevant component list. The components listed in Table V were used based on experience from pilot plant operations and simulations using other larger sets of chemical components. The thermodynamic data were taken from Lindberg [17], disregarding the interaction parameters because the thermodynamic model does not include interactions.

The reactor energy balance is solved in an outer loop for oxygen supply or equilibrium temperature (heat losses are accounted for). This numerical problem is considerably simpler and is solved by a safe-guarded secant method [18]. The thermodynamic equilibrium model includes functionality to use user-specified concentrations for some components, primarily methane and hydrogen sulfide. The resulting gas and smelt composition calculated when this possibility is used is an equilibrium composition, given the fixed or empirically calculated concentrations.

Boundary conditions and constraints
The numerical study consists of six CFD calculations, three thermodynamic equilibrium calculations using FactSage, and three using SIMGAS. The boundary conditions for all the calculations were taken as the measured values obtained from the DP-1 process monitoring system during the experimental campaign. Notice that in the CFD model, H₂S is not part of the reaction scheme (Reactions (1-8)); instead, it is treated as an inert and specified in the material description (Table IV). A similar simplification is made for Na₂CO₃ and NaOH. Currently, the CFD model predictions for CH₄ concentration are far below the measured values, presumably as a result of an improper description of the reaction kinetics. To investigate the influence of methane concentration on gas composition and temperature, part of the CH₄ was treated as inert in three of the CFD calculations (Tables III and IV).

Thermodynamic equilibrium calculations were performed in order to determine the gas composition if all reactions (gas and particle phase) would proceed all the way to equilibrium and used for comparison with the CFD results. As a reference, equilibrium calculations using FactSage were performed at the predicted outlet temperature obtained from CFD. The inlet composition was specified according to Table

<table>
<thead>
<tr>
<th>CFD Proximate Analysis</th>
<th>Case</th>
<th>Specie</th>
<th>% wt</th>
<th>% wt</th>
<th>% wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
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<td>H₂O(l)</td>
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<td>24.8</td>
<td>24.8</td>
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<tr>
<td>Volatiles</td>
<td></td>
<td>H₂S(g)</td>
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<td>1.5</td>
<td>1.4</td>
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<tr>
<td></td>
<td></td>
<td>CO(g)</td>
<td>5.9</td>
<td>5.9</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO₂(g)</td>
<td>9.3</td>
<td>9.2</td>
<td>9.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H₂(g)</td>
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<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH₄(g)</td>
<td>1.18</td>
<td>0.60</td>
<td>0.33</td>
</tr>
<tr>
<td>Fixed carbon</td>
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<td>C(s)</td>
<td>11.8</td>
<td>11.8</td>
<td>11.8</td>
</tr>
<tr>
<td>Ash</td>
<td></td>
<td>Na₃SO₄(l)</td>
<td>10.0</td>
<td>11.0</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na₃S(l)</td>
<td>0.7</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na₂CO₃(l)</td>
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</tr>
<tr>
<td></td>
<td></td>
<td>NaOH(l)</td>
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<td>1.4</td>
<td>1.4</td>
</tr>
<tr>
<td>HHV MJ/kg</td>
<td></td>
<td>12.62</td>
<td>12.60</td>
<td>12.60</td>
<td></td>
</tr>
</tbody>
</table>

IV. Proximate analysis for black liquor used in the CFD calculations.

V. Components used in the thermodynamic model of the system.

---

**Table V**

<table>
<thead>
<tr>
<th>Specie</th>
<th>% wt</th>
<th>% wt</th>
<th>% wt</th>
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</thead>
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<tr>
<td>H₂S</td>
<td>Na₂CO₃</td>
<td>NaOH</td>
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</tr>
<tr>
<td>CO₂</td>
<td>NaOH</td>
<td>NaCl</td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>Na₂SO₄</td>
<td>NaHS</td>
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</tr>
<tr>
<td>H₂</td>
<td>K₂CO₃</td>
<td>K₂S</td>
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</tr>
<tr>
<td>Na₂S</td>
<td>KOH</td>
<td>KCl</td>
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</tr>
<tr>
<td>Na₂CO₃</td>
<td>K₂SO₄</td>
<td>Cl⁻</td>
<td></td>
</tr>
</tbody>
</table>

is a small difference in the experimentally obtained heating value (Table II) and the modeled heating values. To ensure consistency between the experimental results and the model, pyrolysis was treated as a multiphase reaction, with the heat of reaction chosen so that the modeled and experimental heating value became equal.

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Thermodynamic equilibrium calculations were performed in order to determine the gas composition if all reactions (gas and particle phase) would proceed all the way to equilibrium and used for comparison with the CFD results. As a reference, equilibrium calculations using FactSage were performed at the predicted outlet temperature obtained from CFD. The inlet composition was specified according to Table

---

V. Components used in the thermodynamic model of the system.
GASIFICATION

RESULTS

Figure 4 shows the typical temperature distribution obtained from the CFD model. Notice that in the high oxygen-to-black liquor equivalence ratio case, the high temperature region stretches further down in the reactor and is significantly wider. In the rest of the reactor, the temperature is relatively uniform, particularly in the lower parts close to where the experimental samples were collected.

The cold regions in the upper part of the reactor can be explained by the heat absorbed by the droplets in the drying step implemented in the CFD model (Fig. 5). The right part of Fig. 5 also shows the large recirculation zone that is characteristic for this type of gasifier. In Fig. 6, the dry and nitrogen free molar fractions of CH₄ and H₂S (minor gas components) are presented as a function of oxygen-to-wet black liquor mass flow rate ratio (Table I). The methane concentration was prescribed as described previously in one set of the CFD calculations and in one set of the thermodynamic equi-

<table>
<thead>
<tr>
<th>Case</th>
<th>Method</th>
<th>Temperature</th>
<th>Constrained H₂S</th>
<th>Constrained CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 0 +</td>
<td>Thermodynamic</td>
<td>CFD outlet temperature</td>
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<td>No</td>
</tr>
<tr>
<td></td>
<td>equilibrium</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>FactSage</td>
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<tr>
<td>- 0 +</td>
<td>Thermodynamic</td>
<td>Energy equation</td>
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<tr>
<td></td>
<td>equilibrium</td>
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<td></td>
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</tr>
<tr>
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</tr>
<tr>
<td>- 0 +</td>
<td>CFD</td>
<td>Energy equation</td>
<td>Yes</td>
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<tr>
<td>- 0 +</td>
<td>CFD</td>
<td>Energy equation</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

VI. Numerical method and case description; boundary conditions not specified are according to Table I and Table II.
The thermodynamic equilibrium calculations performed with FactSage show a clear divergence from the experimental results, as do the CFD calculations with no restrictions on methane.

**Figure 7** presents the dry and nitrogen free molar fraction of the main gas components (CO, CO₂, and H₂). The general trends (decreasing/increasing concentration) are predicted by both the CFD model and the two equilibrium models, at least for the two points with higher oxygen-to-black liquor mass flow rate ratio. At the lower oxygen-to-black liquor ratio, the solution obtained with FactSage with no constraints on CH₄ or H₂S deviates from the trend and predicts approximately the same CO level as obtained at the middle oxygen-to-black liquor ratio. The values obtained by the CFD model (gas composition) are taken as field values from the calculated position of the sampling probe tip.

The left graph of **Fig. 8** shows the reactor outlet temperature obtained from the in-house thermodynamic equilibrium code and the CFD calculations. The right graph in Fig. 8 shows the fixed carbon conversion for the two CFD models. Notice that there is a significant difference in fixed carbon conversion. When CH₄ is included as an inert, the fixed carbon conversion increases approximately 8% (relative) for the lowest oxygen-to-black liquor mass flow rate ratio. Both thermodynamic equilibrium codes predict 100% fixed carbon conversion and are not shown.

There are only small variations in the smelt composition (Table VII) for the main species (Na₂, CO₃, and Na₂S approximately ±3 % units on mass basis) when varying λ and assuming thermodynamic equilibrium with constraints on CH₄ and H₂S. Furthermore, the smelt composition obtained using thermodynamic equilibrium is in good agreement with the one obtained from the CFD model using the least squares method on the simplified material description described previously.
DISCUSSION

When part of CH4 is included as inert in the calculation, the predictions show much better agreement with the experimentally obtained values compared to the case where no inert CH4 is considered. This is valid for both the equilibrium and CFD calculations. If CH4 and H2S are not specified but calculated using thermodynamic equilibrium, CH4 concentration in the dry, nitrogen free gas is ~0.2% and H2S is ~2.8 % for \( \lambda = 0.44 \). This also has an effect on the major gas components, with the most predominant difference at the low temperature case (\( \lambda = 0.40 \)). The major gas components, when predicted by CFD, are close to equilibrium (within 5% by comparing with the equilibrium constant). Hence, given the good agreement with the experimental data (relative error less than 5%) it could be argued that the major gas components are at or close to equilibrium and the main mechanism is the water gas CO shift reaction. Furthermore, H2S and CH4 are not at thermodynamic equilibrium (cannot be predicted by a thermodynamic equilibrium code) and the dominating mechanisms are not adequately described in the CFD model. Given that the CFD predictions show good agreement (when H2S and CH4 concentrations are prescribed) with the experimentally obtained results, it is possible that the flow field is also adequately predicted. However, this remains to be verified by further experiments.

There is a significant difference in fixed carbon conversion between the performed CFD calculations (Fig. 8). This is particularly true for the low lambda (i.e., low temperature) case when all of the available CH4 is allowed to react, and the fixed carbon conversion is as low as 90.5%. This should be compared to 97.2% for the case when CH4 concentration in the gas is constrained. For the high temperature (i.e., high lambda) case, the fixed carbon conversion is 99.7% for both the CFD model descriptions. In the high temperature case, the temperatures are also very similar between the two CFD models, which could explain the similarities in fixed carbon conversion. It is worth mentioning that, during normal operation of the gasifier, the fixed carbon conversion is very close to 100% because no char or soot is detected in the green liquor or the green liquor dregs.

Figure 4 shows the temperature distribution obtained using CFD. The spreading of the hot region (flame region) increases significantly when lambda is increased. It is possible that the hot region is even longer in the real reactor, given the deficiencies in the k-\( \varepsilon \) turbulence model, where the spreading rate is over predicted for round jets [21]. In the lower part of the reactor, the temperature appears to be rather uniform, which, from an experimental point of view, is encouraging. The lack of temperature gradient would support that the gas composition at the sample point is similar to the one obtained at the outlet [5].

The methane concentration has a significant influence on the gas temperature. If all methane is allowed to react, the reactor outlet temperature is lower compared to when methane is constrained. This becomes apparent for the low oxygen-to-black liquor equivalence ratio case when there is no constraint on methane. The carbon conversion is about 90%, which effectively means that less energy is spent on converting fixed carbon to gas through the gasification reactions. Consequently, if less energy is spent on converting fixed carbon to gas, the gas temperature should be higher. However, this is not observed. The explanation for this is the endothermic steam methane reforming reaction (Reaction 2). Thus, methane that is not oxidized close to the flame will consume energy as it converts to CO and H2. The conversion of methane will reduce the gas temperature, resulting in reduced reaction rates for the gasification reactions with poor fixed carbon conversion as a result. For the highest oxygen-to-black liquor equivalence ratio, the methane concentrations are about three times less than for the low ratio, and the influence from methane concentrations is significantly reduced.

CONCLUSIONS AND FUTURE WORK

From the calculations performed in this work, it is clear that the methane concentration and the conversion of methane have a significant effect on the major gas components. The
methane concentration affects gas temperature because of the endothermic steam methane reforming reaction. In addition, the steam methane reforming reaction contributes to a displacement of the major gas components, because one mole of methane reacting with water vapor will result in three moles of H₂ and one mole of CO. In summarizing this work, the following conclusions can be drawn:

- The main gas components can be predicted both with the present CFD model and thermodynamic equilibrium if CH₄ and H₂S concentrations are prescribed.
- The CH₄ concentration in the gas has a significant influence on the main gas components (H₂, CO, CO₂).
- The fixed carbon conversion increases when part of the methane is treated as inert.
- CH₄ and H₂S are not in equilibrium in the DP-1 black liquor gasifier.
- The main gas components are close to equilibrium at the outlet of the DP-1 black liquor gasifier.

In the future work, the focus should be on implementation of a more detailed mechanism for the formation and conversion of H₂S and CH₄ in the CFD code.

**ACKNOWLEDGMENTS**

The authors of this paper would like to thank the Swedish Energy Agency, Mistra, Smurfit Kappa Krutfliner AB, SCA Packaging AB, Södra Cell AB, Sveaskog AB, Chemrec AB, and the County Administrative Board of Norrbotten for funding this work through the BLG II research program.

**LITERATURE CITED**

High pressure, high temperature black liquor gasification can be a complement or a substitute to the conventional recovery boiler. The technology is just on the verge of being fully commercialized and scale-up operation is in progress. To aid with optimization and scale-up, reliable computational tools are of great importance.

In this work, two different types of computational models (CFD and thermodynamic equilibrium) have been used to predict the gas composition inside the gasification reactor. The predictions have then been compared to experimental data (obtained by our research group) and show very good agreement. Surprisingly, small concentrations of methane have a large influence on the temperature in the gasification reactor. Consequently, this will affect both the main gas components and the fixed carbon conversion.

The large differences in time and length scale between the convective flow (order of reactor dimensions) and the chemical reactions (order of flame thickness) makes modeling of gasification or combustion challenging. In this work, we were able to overcome the problem by careful selection of time steps for the momentum, continuity, and energy equations, respectively. In the future, the CFD model will be further refined so it can be used to accurately predict the behavior of entrained flow gasifiers of arbitrary size using different kinds of fuels.

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Paper V

Carlsson P., Iisa K., Gebart R., Predicting the outlet gas composition from a black liquor gasifier using CFD – Comparison with experiments. Submitted to Energy & Fuels
Predicting the outlet gas composition from a black liquor gasifier using CFD – Comparison with experiments

Per Carlsson1,3*, Kristiina Iisa2, Rikard Gebart1,3

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2National Renewable Energy Laboratory, Golden CO
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ABSTRACT
Pressurized entrained flow high temperature black liquor gasification can be used as a complement or a substitute to the Tomlinson boiler used in the chemical recovery process at Kraft pulp mills. The technology has been proven in development scale but there are still no full scale plants. This work is intended to aid in the development by providing computational tools that can be used in scale up of the existing technology. In this work an existing CFD model describing the gasification reactor is refined. First 1-D plug flow reactor calculations are performed to aid in the refinement, particularly to judge the validity (by comparing with a more comprehensive reaction mechanism) of the global homogeneous reaction mechanism used in the CFD calculation in the temperature range considered. Later influence of the pyrolysis gas composition and reaction mechanism on the gasifier outlet composition is evaluated using CFD. Finally the results from the updated CFD model are compared to experimental results in which pressure, oxygen to black liquor equivalence ratio, and residence time have been varied. The results show that the updated CFD model can predict the main gas components (H₂, CO, CO₂) within an absolute error of 2.5 %. CH₄ can be predicted within an absolute error of 1 % and char conversion within an absolute error of 11%. The results also show that most of the trends when process conditions are varied are captured by the model.

Keywords: CFD, gasification, experiments, black liquor
INTRODUCTION

The tallest chimney at a modern pulp mill is most certainly the one connected to the recovery boiler. In the recovery boiler concentrated black liquor is burnt to recover the heat and the cooking chemicals used in pulp making process as an ash residue. The black liquor is a highly viscous fluid with a higher heating value of about 12 MJ/kg (can be compared to ~45 MJ/kg for crude oil). The black liquor consists of roughly 1/3 water and 2/3 solids. The solids are mainly the spent cooking chemicals (Na2S, NaOH, Na2CO3, and Na2SO4), dissolved lignin, dissolved carbohydrates, and a small portion of inorganic compounds found in the wood. The cooking chemicals which make up about 1/3 of the mixture result in an elevated pH of about 12-14 [1]. An alternative to recovery boiler which may increase the thermal and electrical efficiency of the recovery cycle is gasification [2]. There are different black liquor gasification technologies [3] and this work will focus on high temperature, pressurized, entrained flow black liquor gasification.

Since 2005 the technology vendor Chemrec has been operating a 3 MWth pressurized entrained flow high temperature black liquor gasification plant named DP-1 [4]. The plant, which now has an accumulated operating time of approximately 12 000 h, is adjacent to the Smurfit Kappa Kraftliner pulp and paper mill in Piteå, Sweden. Just recently, a catalytic plant was commissioned in conjunction with the gasification plant to produce Dimethyl Ether (DME) which is a gaseous diesel substitute [5] from the syngas produced by the gasification process. In previous work gas samples were withdrawn from the hot gasification reactor [6] using a water-cooled sampling probe [7]. During the experimental campaign several operating conditions, such as temperature, residence time and pressure were varied. Furthermore, in a recent study [8] these experimental results were compared to Computational Fluid Dynamics (CFD) predictions in which the oxygen to black liquor equivalence ratio was varied. The results showed that methane could not be predicted adequately at the outlet of the gasifier. The experiments showed a methane concentration ranging from 0.5 % mol to about 2.5 % mol whilst the model predicted 0%. The discrepancy in the CH4 concentration led to large deviations in the main gas component concentrations. In order to resolve this, the CH4 concentration was prescribed by treating part of the CH4 as inert, and reasonable predictions for the main gas components were obtained.

The objective of the current work is to improve the CFD model by enhancing the model for methane transformation. The global reaction mechanism used in the previous work is compared to a more comprehensive reaction mechanism in 1-D plug flow reactor simulations. Then, the influence of the pyrolysis gas composition on the gasifier outlet composition is
evaluated using CFD. Finally the results from the updated CFD model are compared to experimental results in which pressure, oxygen to black liquor equivalence ratio (from here on equivalence ratio), and residence time have been varied. The main goal has been to make the CFD reactor model less dependent on prescribed model parameters (prescribed methane concentration) and improve the predictions for a wider range of operating conditions while maintaining numerical stability and simplicity.

EXPERIMENTAL
The DP-1 black liquor gasification plant is described schematically in Figure 1. The main parts are the refractory lined 3 MWth oxygen blown gasification reactor, the quench, and the gas cooler. In the reactor, preheated (~140 °C) black liquor is injected through a centrally placed spray burner nozzle at the top of the gasifier, together with oxygen and a small portion of nitrogen (about 20 % of the oxygen mass flow rate). At elevated pressure (normal operating pressure, 31 bar) and a temperature of about 1000 °C the black liquor is gasified to form H2O, CO2, CO, H2, H2S, CH4 and a liquid ash. The ash in the black liquor which makes up approximately 30 % of the virgin fuel melts due to the high temperature and is recovered in the quench located downstream, directly underneath the gasification reactor. Here, the gas and the smelt are rapidly cooled by water spray nozzles and separated so that the smelt is dissolved in water in the bottom of the quench forming green liquor which may be returned to the pulp mill for further recovery treatment. Downstream the quench is the gas cooler, which is designed to condense the water vapor in the gas and at the same time remove carry-over particulates and condensable hydrocarbons that were not trapped in the quench. To remove the sulphur components in the syngas (mainly H2S) both a common sulphur removal technique [9] and a novel method based on short time contactors have been used [10]. The DP-1 gasifier is approximately 2.3 meters in height and 0.6 meters in diameter. During the experimental campaign gas samples were collected in the lower part of the gasification reactor approximately 0.6 m above the outlet. The samples were obtained using a specially designed water-cooled quench probe [7]. The collected gas samples were analyzed with respect to CH4, CO, CO2, H2, N2, H2S, COS, and O2/Ar using a Varian CP-3800 gas chromatograph. During the experimental campaign several different process parameters were varied (see Tab. I) and these variations resulted in variations in operating conditions (pressure, temperature and residence time). During the experimental campaign a base operating condition was established at 28 bar and a temperature of about 1000 °C which for the liquor composition (showed in Tab. II) used in the experiments corresponded to an oxygen to black liquor
equivalence ratio (defined as \( \lambda = \frac{x_{\text{O}_2}}{x_{\text{fuel}}} / \frac{x_{\text{O}_2,\text{stoich}}}{x_{\text{fuel,stoich}}} \), where \( x \) is mol fraction) of 0.434. As can be seen in Tab. I this base operating condition can be found in the high pressure case (+P) and in the medium temperature case (0\( \lambda \)). The normalized gas residence time showed in Tab. I is based on a plug flow assumption, with the base operating conditions set to unity. In this case, high pressure in combination with low mass flow rates results in a long gas residence time and vice versa.

**Numerical**

*The CFD model*

The current CFD model and its material description have been extensively discussed by Marklund et al. [11] and Carlsson et al. [8] and will therefore only be summarized here. The reactor geometry was modeled as a 2D slice using periodic azimuthal boundary conditions based on rotational symmetry. The wall heat losses were set to 90 kW evenly distributed along the refractory wall, based on previous estimates. The burner was modeled as a simplified spray burner with concentrical annular inlets where oxygen and discrete black liquor droplets enter the gasifier at a prescribed range of angles and velocities. The two-phase flow consisting of dispersed black liquor particles and gases were modeled using the Euler – Lagrange formulation [12]. The black liquor spray was represented by 1003 discrete particles having a fitted Rosin Rammler distribution of power 2 and a characteristic size of 200 \( \mu \text{m} \). The droplet size distribution and flow velocity are consistent with data (unpublished) from nozzle experiments measured by phase Doppler anemometry [13]. Turbulence was modeled with the k-\( \varepsilon \) model using scalable wall functions [14] together with a turbulent dispersion model [15] to introduce turbulence effects on the black liquor particles. Radiative heat transfer was modeled using the Discrete Transfer radiation model by Lockwood and Shah [16] treating the wall as optically smooth with a radiative emissivity of 0.5. The absorption coefficient for the gas was calculated as the mass weight average of the participating species. To ensure consistency between the experimental and modeled heating value, heat of reaction for pyrolysis in the model was taken as the difference between the modeled and experimental heating value. Drying, pyrolysis, char gasification and smelt formation reactions were modeled as showed in Tab. III using the reaction mechanisms and coefficients described by Marklund [13]. The model was implemented in the commercial CFD software package Ansys CFX [1] where the multiphase reactions were implemented in user defined FORTRAN subroutines.
Plug flow reactor calculations

In order to select an appropriate gas phase reaction mechanism for the CFD model, Plug Flow Reactor (PFR) calculations were performed in the chemical kinetics program Cantera [18] with the GRI-Mech 3.0 [19] used as a reference mechanism. The mechanisms considered for the CFD model are the 4 step, 6 species global reaction mechanism developed by Jones and Lindstedt [20], which was used in our previous modeling work [8], and a simplified oxidation mechanism [21]. Reactions R1 to R4 shown in Tab. III constitute the Jones and Lindstedt mechanism and the kinetics used in the CFD model was also taken from the paper by Jones and Lindstedt. The model has been developed for the combustion of methane, and includes reactions for hydrogen oxidation, methane oxidation and steam reforming, and the water gas shift reaction. The oxidation mechanism omits the steam methane reforming reaction (SMR, R2) and consists of reactions for hydrogen, CO, and methane oxidation, and the water gas shift reaction (reactions R1 and R3 through R5). In this case the kinetics were taken from [1] for reaction R1 and R5 and from [20] for reaction R3 and R4. The Jones and Lindstedt mechanism was compared to GRI-Mech with respect to methane conversion in plug flow reactor calculations performed at isothermal conditions with the following inlet molar gas composition: CH4: 10%, CO2: 20% CO: 20%, H2O: 25%, H2: 25%. The pressure was set to 28 bar and the temperatures to: 1273, 1400 and 1650 K.

Influence from variations in CO/CO2 in the pyrolysis gas and reaction mechanism

The black liquor ultimate analysis was simplified and converted into species using the assumptions in Marklund et al. [11] and the method described in Carlsson et al. [8]. The CO/CO2 molar ratio in the pyrolysis gas and the ratio of fixed carbon and the pyrolysis gas carbon are prescribed parameters. As can be seen in Figure 2 both ratios influence the amount of methane that is released during pyrolysis. Consequently, this will have an effect on how much methane is present in the syngas coming out from the reactor.

The influence of the pyrolysis assumptions was investigated with CFD by calculating the outlet gas composition using three different CO/CO2 ratios, 1, 8 and 16 (Tab. IV). The reaction mechanisms used in the calculations were the Jones and Lindstedt mechanism with extinction temperatures (forces reaction rate to zero if temperature is below the preset value) set to 1273 and 1400 K for the steam methane reforming reaction (R2), and the oxidation mechanism described above. The results from these calculations were then compared to the experimental values for the base operating condition (0, see Tab. I).
Influence from variations in process conditions

The different operating conditions presented in Tab. I were modeled by CFD simulations. When the process conditions were varied the CO/CO₂ was set to unity and the carbon char/gas ratio to 50%. The boundary conditions used in the CFD simulations were taken as the process values obtained from the DP-1 process monitoring system showed in Tab. I. The Jones and Lindstedt mechanism with the addition of an extinction temperature set to 1400 K on the steam methane reforming reaction was used as the homogeneous reaction mechanism. The Jones and Lindstedt mechanism was implemented in CFD code with the water gas shift reaction (R4) modeled using the Finite Rate Chemistry model (FRC) and the irreversible reactions using the combined eddy dissipation/FRC-model [1]. Currently, the CFD model does not include a reaction mechanism for H₂S; instead it is treated as an inert. The concentration of H₂S at the outlet will be determined by the pyrolysis gas composition showed in Tab. IV and to some extent dilution.

RESULTS

Plug flow reactor calculations

The PFR calculations were done in order to simulate regions in the gasification reactor where the temperature is still relatively high but all oxygen is depleted. The inlet gas composition was set to a typical syngas composition and the effects of temperature were investigated. In Figure 3 the evolution of methane is showed as function of residence time in an isothermal plug flow reactor and a total residence time of 5 s. In the GRI mechanism, methane starts to reform at about 1400 K. After 5 s only 5% have been converted into other species (mainly CO and H₂). At 1550 K (not showed in Figure 3), about 60% have been reformed and at the highest temperature, 1650 K, almost all methane is reformed. The Jones and Lindstedt mechanism shows a significantly higher reformation rate. At 1400 K, about 85% of the methane has been reformed, which should be compared to 5% for GRI-Mech. The conversion of the methane has an immediate effect on the major gas components as can be seen in Figure 4. The results also show that the water gas shift reaction (R4) is significantly faster in the Jones and Lindstedt mechanism than the reactions determining the major gas components in GRI-Mech. However, for the highest temperature (1650 K) the agreement is much better both for methane prediction and for the main gas components. The pure oxidation mechanism does not include the reformation of methane and is therefore not showed.
Influence from variations in CO/CO₂ and reaction mechanism

The reaction mechanisms were further investigated using CFD and the results are presented in Tab. V. Three reaction mechanisms were tested: the Jones and Lindstedt mechanism with extinction temperatures set to 1273 and 1400 K for the steam methane reforming reaction (R2), and the oxidation mechanism. As can be seen in Tab. V there is a significant difference in the outlet methane concentration, ranging from 0 % mol to just above 5% mol depending on the CO/CO₂ ratio and the reaction mechanism. The values should be compared to the experimentally obtained value of 1.40% mol on dry nitrogen free basis. The Jones and Lindstedt mechanism with extinction temperature set to 1400 K and a CO/CO₂ ratio of 1 gives similar predictions as the pure oxidation mechanism with the CO/CO₂ ratio set to 16. For the Jones and Lindstedt mechanism, about 90% of the methane (released during pyrolysis) is reformed and oxidized to main components. For the oxidation mechanism this value is about 60 %. Even though the two reaction mechanisms perform similarly the Jones and Lindstedt model with the SMR extinction temperature set to 1400 K and a CO/CO₂ ratio set to unity was chosen for the CFD calculation in which process conditions were varied.

Influence from variations in process conditions

The results from the process conditions variation are showed in Tab. VI (with relative error) and Figure 5 (showing trends in graphs). As can be seen in Tab. VI the predictions of the main gas components show an overall good agreement; absolute values are within 2.5%, and relative errors for major gas components within 9.0%. The lower heating value is predicted very well for all the cases and the largest relative error can be found for the low temperature (-λ) case at -4.6%. The average relative error (for the heating value) for all the cases is about 1.7 %.

In the pressure variation experiments, the predictions for the main gas components are within a relative error of approximately 5 %. However, the trends are not predicted for CO and CO₂. The experimentally obtained values show a clear decrease in CO₂ and increase in CO when pressure is increased and this is not captured by the model. The trend in CH₄ also suggests that the middle pressure point (0P 21 bar) is the operating condition that deviates from the trend. The relative error in CH₄ is similar for the low and high pressure case but is about two times as large for the medium pressure case. The trend in H₂ concentration is predicted, i.e. an increase in concentration with an increase of pressure. H₂S show the second largest relative error at about 25 %. H₂S is treated as an inert in the model and hence will not be influenced by operating conditions. The outlet concentration is instead dictated by the initial release of
H2S (see Tab. IV). The char conversion and temperature are the highest at the medium pressure point at 98.8 % and about 1245 K at the outlet respectively (Figure 6).

When the equivalence ratio is varied the predictions are encouraging. The increase in CO with increased equivalence ratio is captured as well as the decrease in H2. In the experiments an increase in CO2 was observed, which is not captured by the model. However, the increase in CO2 observed in the experiments is relatively small, about 0.7 percentage points which corresponds to approximately two standard deviations. The largest relative error can be found for methane in the low temperature case but encouragingly the error is significantly smaller at the higher equivalence ratios. The trend in CH4 is predicted correctly. Figure 6 shows that an increase in equivalence ratio leads to an increase in char conversion and the difference is about 10 percentage points between the high and low equivalence ratio cases. The mean, outlet and probe position temperatures all increase when the equivalence ratio is increased.

The residence time experiments were conducted at a constant pressure, that is, an increase in residence time was achieved by decreasing the black liquor mass flow rate and vice versa. Since the thermal power is also changed when the black liquor mass flow rate is varied the influence of the wall heat losses will be greater at long residence time/low black liquor mass flow rate. However, during the experiments the temperature inside the reactor was kept at around 1000 °C by changing the equivalence ratio. It was assumed that the wall heat losses will be relatively constant (since ΔT is constant cross the reactor wall) regardless of black liquor mass flow rate. The wall heat losses will, however, be a greater portion of the thermal throughput. The short and medium residence times have almost equal equivalence ratios (see Tab. I), and the methane concentration is almost constant for these two residence times. The model predicts this trend fairly well. However, at the longest residence time the trend is lost even though the absolute value is closer to correct. The predicted methane has the largest relative error in the short and mid residence time cases at around 45 %. This error is also reflected in the prediction of CO with a relative error of 9% at the shortest residence time. This is the largest error for the main components in the entire set of simulations. Because of the discrepancies in CH4 predictions, the trend predictions for the main gas components are not as clear. The trend in CO2 is somewhat captured with fairly constant values at the short and medium residence time and an increase at the longer residence time. For CO and H2 there is no clear trend from the model. The char conversion decreases at the longer residence time compared to the shortest as do all the temperatures.
DISCUSSION

The initial PFR calculations performed in this work confirmed that the reformation of methane is significantly overpredicted when using the Jones and Lindstedt mechanism in this temperature range. This comes as no surprise since the Jones and Lindstedt mechanism was developed for combustion. In a supplementary study (not presented here) the Jones and Lindstedt mechanism was compared to GRI-Mech in a counter flow oxygen methane jet flame and it performed fairly well given its simplicity. Additional PFR calculations were performed at different inlet gas composition with similar results (not presented here); the Jones and Lindstedt model showed significantly higher reformation rate of methane than GRI-Mech at gasification conditions in the medium temperature range (1150 K < T < 1500 K). This probably explains why in our previous work [8] we were not able to predict the methane concentration accurately in the DP-1 black liquor gasifier.

The conversion of methane in a plug flow reactor with gas composition representative of syngas has been experimentally investigated by Valin et al. [23] who obtained about 18 % conversion at a residence time of 2.1 s and a temperature of 1400 K. In the CFD-simulations 1400 K was set as the extinction temperature for the SMR reaction in order to get reasonable predictions. This is slightly higher than the temperature at which negligible conversion was obtained by Valin et al. It is possible that an even higher extinction temperature would result in improved predictions of the CH₄ concentrations. However, 1400 K was considered a reasonable value based on the results from the PFR calculations and the experimental results obtained by Valin et al [23]. In an early stage of the present work a more comprehensive scheme [24] was considered for the CFD model calculations. However, this approach turned out to be computationally too expensive and difficult to control regarding numerical stability. Hence, the current extinction temperature approach was chosen instead even if there are some uncertainties around the reaction mechanisms regarding the conversion of methane.

Furthermore, there are catalytic effects present and uncertainties in the pyrolysis gas composition, which in the real case involves several hydrocarbon species [25] that will affect the outlet gas composition. The composition of the pyrolysis gas and the char yield has been examined by Sriraroenchaikul et al. [25, 26, 27] in a laminar entrained flow reactor. At 1000 °C about 65% [27] of the dry black liquor could be found as char residue; in the model this value is about 70% which is of similar order. The CO/CO₂ ratio in the pyrolysis gas has a temperature and residence time dependency [26]. Furthermore, since CO and CO₂ may be formed from secondary reaction in the gas phase it is difficult to define an accurate single value for the CO/CO₂ pyrolysis gas ratio. Thus, even if a more comprehensive reaction
scheme had been applied in the present case there is no guaranty that the outlet gas composition would have been predicted more accurately since there are uncertainties in the pyrolysis gas composition.

As can be seen in Tab. V the main gas components can be predicted within a relative error of about 5% when using the Jones and Lindstedt model and the extinction temperature set to 1400 K for the SMR. Similar results were obtained from the oxidation model with CO/CO₂=16. The combined total error, i.e. the sum of all the relative errors for each case and the considered species and heating value presented in Tab. V is also similar for the two models (about 35 %) with a slight advantage for the Jones and Lindstedt model. The two reaction mechanisms are both of first order, i.e. the conversion of methane will be more or less constant at any initial concentration of methane. The results showed that the conversion of methane was about 60 % for the oxidation mechanism and circa 90 % for the Jones and Lindstedt mechanism with SMR extinction temperature set to 1400 K. This was regardless of the pyrolysis gas CO/CO₂ ratio and hence the initial release of methane. The Jones and Lindstedt model was chosen for the process condition variation calculations because it contains the SMR (which may have a strong influence on the results when the process conditions are varied) and because the Jones and Lindstedt mechanism predicts the flame reasonably.

When the process conditions are varied the largest error for the main gas components can be found in the short residence time experiment (see Tab. VI and Figure 5). The absolute error for CO is 2.5% which corresponds to 9% on a relative basis. For the same case, the methane prediction also shows the largest relative error of about 45%. The discrepancy is believed to be due to errors in the assumed heat loss for this case. Figure 7 shows the predicted methane concentrations and char conversions against the predicted outlet temperatures and equivalence ratios. The char and CH₄ conversions, as can be seen in Figure 7 both increase with increased temperature. However, the trend is not as clear when the same results are plotted against the equivalence ratio (right parts in Figure 7). The discrepancies that can be seen for the CH₄ prediction (particularly for the cases 0P, -λ +τ and 0f) may be associated with the wall heat loss. In the simulations the heat loss was assumed constant at 90 kW (uniformly distributed at the wall) for all the cases. A constant wall temperature would yield a constant ΔT cross the refractory and hence a constant heat flux but this may not be the case since the temperature measurement may be wrong. The temperature is measured with wall mounted thermocouples which may not measure a representative temperature, rather a mix of radiation from the flame, the walls, the gas and convection from the gas. In future work it may be more appropriate to
include the refractory in the simulations (and use a fixed temperature boundary condition at the outside of the refractory) to see how it will influence the results, particularly the heat distribution and heat loss. The experimental results imply that the heat loss is smaller at reduced thermal power/black liquor flow rate. If the heat loss is smaller this would result in higher reactor temperature and hence reduced methane concentration in the outlet gas.

The H$_2$S released during pyrolysis was constant in all calculations (see Tab. IV). This will influence the results, not just for the H$_2$S concentration. Marklund [28] showed that an increase of H$_2$S in the gas will effectively lead to a reduced reactor temperature and thus char conversion since more of the char is converted through the gasification reactions (MR3 and MR4) than by the sulphate reduction reaction (MR5).

During the experimental campaign the char conversion in the DP-1 black liquor gasifier was very close to complete since no char was found in the green liquor or the green liquor dregs. However, the model is not able to predict full conversion for any of the simulated cases. The char conversion for the base case (0, +P) predicted by the model is about 96%, which results in the same order of relative error as for the main gas components. The predicted char conversion for the low temperature case (-) is about 88% which is significantly lower than the experimentally obtained one (estimated to 99.95%). This may be a result of uncertain char conversion rates but does not hinder that the model is used for optimization or scale-up. The low temperature operating point (-) is not favorable in the DP-1 gasifier (may cause fouling in downstream equipment). Hence, even if the predicted char conversion is lower than in the DP-1 gasifier the predictions still provide useful information for finding “safe” operating conditions for a larger gasifier or for optimization.

The simulations carried out in this work were done at operating conditions where data points were available. It is possible that additional simulations both between these points and at extremes could provide additional information about operating conditions at which the model seems reliable. In general the model predicts most of the trends and in some cases even the actual values from the experiments. The main goal was to make the CFD reactor model less dependent of prescribed model parameters and improve the predictions for a wider range of operating conditions while maintaining numerical stability and simplicity. This was achieved by using the extinction temperature approach described previously. A comparison with experiments has showed that the model is reliable and can be used for optimization or scale up as long as the pressure, equivalence ratio and residence time are kept within the boundaries studied. This however, does not limit the model’s validity for higher thermal powers, i.e. reactor sizes.
CONCLUSIONS AND FUTURE WORK

In this work, a global reaction mechanism developed by Jones and Lindstedt [20] was compared to GRI-Mech in a 1-D plug flow reactor. The Jones and Lindstedt model was then compared to a global oxidation mechanism using CFD and the influence of the reaction mechanism and initial release of CH₄ was studied. Finally the CFD model was compared to experimental values obtained from an entrained flow high temperature black liquor gasifier. From the results obtained the following conclusions can be drawn.

PFR calculations

- The agreement between the Jones and Lindstedt model and GRI-Mech in a plug flow reactor is generally good if the temperature is above 1650 K.
- The Jones and Lindstedt model overpredicts the reformation of CH₄ if the temperature is below 1650 K.

Influence from variations in CO/CO₂ and reaction mechanism

- The CO/CO₂ ratio and the gas/char carbon ratio will have a large influence on the amount of methane that is released during modeled pyrolysis.
- It is possible to use an extinction temperature to separate the flame from the post flame region.

Influence from variations in process conditions

- When pressure is varied from 16 bar to 28 bar the main gas components (H₂, CO and CO₂) can be predicted within a relative error of 5.3%, the CH₄ within a relative error of 37.4% and the heating value of the gas within a relative error of 2.7%.
- When equivalence ratio is varied from 0.396 to 0.452 the main gas components (H₂, CO and CO₂) can be predicted within a relative error of 4.7%, the CH₄ within a relative error of 35.2% and the heating value of the gas within a relative error of 4.6%.
- When residence time (normalized) is varied from 0.65 to 1.28 the main gas components (H₂, CO and CO₂) can be predicted within a relative error of 9.0%, the CH₄ within a relative error of 45.6% and the heating value of the gas within a relative error of 1.4%.
- The resulting char conversion obtained with the CFD model increases with increased temperature.
- The resulting CH$_4$ conversion obtained with the CFD model increases with increased temperature.
- Most of the trends are predicted by the CFD model.

*Future work*
- Develop a model for the distribution of sulphur between the particle and gas system.
- Include the refractory lining and pressure vessel so a constant temperature boundary condition can be used at the walls instead of the current constant heat flux.
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### Tab. II. Black liquor ultimate analysis used in the experiments

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**Proximate Analysis**

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<td>Fixed carbon</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>HHV MJ/kg</td>
<td>12.57</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*by difference, **by difference from uncertainties in participating elements using extremes*
Tab. III. Reactions considered in the CFD-model, R: homogeneous reactions. MR: Heterogeneous reactions. The Jones mechanism is reaction R1-R4 the combustion mechanism is reaction R1, R3, R4 and R5.

<table>
<thead>
<tr>
<th>REACTION</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$</td>
<td></td>
</tr>
<tr>
<td>R2</td>
<td>$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$</td>
<td></td>
</tr>
<tr>
<td>R3</td>
<td>$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$</td>
<td></td>
</tr>
<tr>
<td>R4</td>
<td>$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$</td>
<td></td>
</tr>
<tr>
<td>R5</td>
<td>$\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$</td>
<td></td>
</tr>
<tr>
<td>MR1</td>
<td>$\text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{O} (g)$</td>
<td></td>
</tr>
<tr>
<td>MR2</td>
<td>Volatiles $\rightarrow a\text{H}_2\text{S} + b\text{CO} + c\text{CO}_2 + d\text{H}_2 + e\text{CH}_4$</td>
<td></td>
</tr>
<tr>
<td>MR3</td>
<td>$\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$</td>
<td></td>
</tr>
<tr>
<td>MR4</td>
<td>$\text{C} + \text{CO}_2 \rightarrow 2\text{CO}$</td>
<td></td>
</tr>
<tr>
<td>MR5</td>
<td>$\text{C} + \frac{1}{2}\text{Na}_2\text{SO}_4 \rightarrow \frac{1}{2}\text{Na}_2\text{S} + \text{CO}_2$</td>
<td></td>
</tr>
</tbody>
</table>

*Coefficients $a \rightarrow e$ molar fractions derived from Tab. IV.

Heat of reaction taken as the difference between the experimental and modeled heating value.
Tab. IV. Simplified ultimate analysis and proximate analysis used in the calculations

<table>
<thead>
<tr>
<th>SIMPLIFIED ULTIMATE ANALYSIS</th>
<th>%wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>31.30</td>
</tr>
<tr>
<td>H</td>
<td>3.40</td>
</tr>
<tr>
<td>O</td>
<td>37.34</td>
</tr>
<tr>
<td>N</td>
<td>0.00</td>
</tr>
<tr>
<td>S</td>
<td>5.60</td>
</tr>
<tr>
<td>Na</td>
<td>22.36</td>
</tr>
<tr>
<td>K</td>
<td>0.00</td>
</tr>
<tr>
<td>Cl</td>
<td>0.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PROXIMATE ANALYSIS</th>
<th>Species</th>
<th>CO/CO₂ mol ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
</tr>
<tr>
<td>Moisture %wt</td>
<td>H₂O(l)</td>
<td>24.80</td>
</tr>
<tr>
<td></td>
<td>H₂S(g)</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>CO(g)</td>
<td>5.86</td>
</tr>
<tr>
<td>Volatiles %wt</td>
<td>CO₂(g)</td>
<td>9.20</td>
</tr>
<tr>
<td></td>
<td>H₂(g)</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>CH₄(g)</td>
<td>4.83</td>
</tr>
<tr>
<td>Fixed carbon %wt</td>
<td>C(s)</td>
<td>11.77</td>
</tr>
<tr>
<td>Ash %wt</td>
<td>Na₂SO₄(l)</td>
<td>11.00</td>
</tr>
<tr>
<td></td>
<td>Na₂S(l)</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>Na₂CO₃(l)</td>
<td>27.64</td>
</tr>
<tr>
<td></td>
<td>NaOH(l)</td>
<td>1.42</td>
</tr>
<tr>
<td>HHV MJ/kg</td>
<td></td>
<td>12.60</td>
</tr>
</tbody>
</table>
Tab. V. Experimental and numerical results (CFD), units are % mol and MJ/kg. Influence from CO/CO$_2$ ratio and reaction mechanism on outlet gas composition. The experimental results showed above each column were obtained from [7]. Mechanisms are the Jones and Lindstedt [20] with extinction temperature set to 1273 K and 1400 K on the steam methane reforming reaction (R2 in Tab. III) and the oxidation mechanism (R1, R3, R4, R5).

<table>
<thead>
<tr>
<th>MECHANISM</th>
<th>CO/CO$_2$</th>
<th>CO</th>
<th>H$_2$</th>
<th>CH$_4$</th>
<th>H$_2$S</th>
<th>LHV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>34.3 ± 0.3 %</td>
<td>28.5 ± 0.2 %</td>
<td>34.1 ± 0.2 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Num. Rel. error</td>
<td>Num. Rel. error</td>
<td>Num. Rel. error</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jones and Lindstedt</td>
<td>1</td>
<td>31.5% -8.8%</td>
<td>30.6% 6.9%</td>
<td>36.2% 5.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMR ext. temp 1273 K</td>
<td>8</td>
<td>33.8% -14%</td>
<td>28.2% -11%</td>
<td>36.2% 5.9%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jones and Lindstedt</td>
<td>1</td>
<td>35.1% 2.3%</td>
<td>27.2% -4.9%</td>
<td>34.8% 2.2%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SMR ext. temp 1400 K</td>
<td>8</td>
<td>34.5% 0.5%</td>
<td>27.9% -2.4%</td>
<td>35.4% 3.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxidation of CH$_4$ CO and H$_2$ with water gas shift</td>
<td>16</td>
<td>35.5% 3.2%</td>
<td>27.2% -5.0%</td>
<td>33.8% -0.8%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MECHANISM</th>
<th>CO/CO$_2$</th>
<th>CH$_4$</th>
<th>H$_2$S</th>
<th>LHV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1.40 ± 0.07 %</td>
<td>1.64 ± 0.04 %</td>
<td>7.31 MJ/Kg</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Num. Rel. error</td>
<td>Num. Rel. error</td>
<td>Num. Rel. error</td>
</tr>
<tr>
<td>Jones and Lindstedt</td>
<td>1</td>
<td>0.00% -</td>
<td>1.63% -0.6%</td>
<td>7.80 6.3%</td>
</tr>
<tr>
<td>SMR ext. temp 1273 K</td>
<td>8</td>
<td>7.12% -</td>
<td>1.69% 2.8%</td>
<td>7.34 0.4%</td>
</tr>
<tr>
<td>Jones and Lindstedt</td>
<td>1</td>
<td>1.15% -22.4%</td>
<td>1.71% 3.9%</td>
<td>7.31 0.0%</td>
</tr>
<tr>
<td>SMR ext. temp 1400 K</td>
<td>8</td>
<td>5.48% -156.1%</td>
<td>1.71% 4.1%</td>
<td>7.30 -0.1%</td>
</tr>
<tr>
<td>Oxidation of CH$_4$ CO and H$_2$ with water gas shift</td>
<td>16</td>
<td>5.15% 72.8%</td>
<td>1.83% 10.2%</td>
<td>7.29 -0.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.27% 38.3%</td>
<td>1.76% 6.8%</td>
<td>7.16 -2.1%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.81% 22.6%</td>
<td>1.72% 4.6%</td>
<td>7.36 0.7%</td>
</tr>
</tbody>
</table>
Tab. VI. Experimental and numerical results (CFD), units are % mol and MJ/kg. Boundary conditions are according to Tab. I. The standard deviation (STD) values were obtained from [7].

<table>
<thead>
<tr>
<th>CAMPAIGN</th>
<th>Case</th>
<th>Variations in pressure</th>
<th>Variations in temperature</th>
<th>Variations in residence time</th>
<th>CO2 STD ±0.3</th>
<th>CO STD ±0.2</th>
<th>H2 STD ±0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>-P</td>
<td></td>
<td>-0.2%</td>
<td>1.8%</td>
<td>-4.5%</td>
<td>37.1 36.1</td>
<td>27.4 28.6</td>
<td>33.0 32.7</td>
</tr>
<tr>
<td>0P</td>
<td></td>
<td>-2.8%</td>
<td>3.3%</td>
<td>-2.7%</td>
<td>34.0 35.1</td>
<td>28.4 29.3</td>
<td>33.3 33.7</td>
</tr>
<tr>
<td>+P</td>
<td></td>
<td>3.3%</td>
<td>-1.0%</td>
<td>-1.8%</td>
<td>34.1 34.7</td>
<td>28.5 27.2</td>
<td>34.2 34.8</td>
</tr>
<tr>
<td>-t</td>
<td></td>
<td>-4.5%</td>
<td>2.3%</td>
<td>-2.7%</td>
<td>34.3 35.1</td>
<td>28.5 27.2</td>
<td>34.4 34.8</td>
</tr>
<tr>
<td>0t</td>
<td></td>
<td>-2.7%</td>
<td>-1.0%</td>
<td>-1.8%</td>
<td>34.8 34.5</td>
<td>29.5 29.1</td>
<td>33.4 34.0</td>
</tr>
<tr>
<td>+t</td>
<td></td>
<td>0.4%</td>
<td>-0.4%</td>
<td>0.4%</td>
<td>37.1 37.3</td>
<td>27.5 26.0</td>
<td>32.6 33.6</td>
</tr>
<tr>
<td>-g540</td>
<td></td>
<td>-35.2%</td>
<td>-9.9%</td>
<td>-4.5%</td>
<td>2.72 1.76</td>
<td>1.95 1.76</td>
<td>7.95 7.58</td>
</tr>
<tr>
<td>0g540</td>
<td></td>
<td>-37.4%</td>
<td>4.1%</td>
<td>-4.5%</td>
<td>1.40 1.15</td>
<td>1.64 1.71</td>
<td>7.31 7.31</td>
</tr>
<tr>
<td>+g540</td>
<td></td>
<td>-19.3%</td>
<td>8.8%</td>
<td>-4.5%</td>
<td>0.76 0.72</td>
<td>1.55 1.69</td>
<td>7.17 7.27</td>
</tr>
<tr>
<td>-g306</td>
<td></td>
<td>-45.6%</td>
<td>9.9%</td>
<td>-4.5%</td>
<td>1.44 0.78</td>
<td>1.55 1.70</td>
<td>7.38 7.47</td>
</tr>
<tr>
<td>0g306</td>
<td></td>
<td>-43.2%</td>
<td>16.8%</td>
<td>-4.5%</td>
<td>1.49 0.85</td>
<td>1.47 1.71</td>
<td>7.33 7.39</td>
</tr>
<tr>
<td>+g306</td>
<td></td>
<td>19.2%</td>
<td>10.1%</td>
<td>-4.5%</td>
<td>1.15 1.37</td>
<td>1.62 1.78</td>
<td>6.86 6.96</td>
</tr>
</tbody>
</table>

Variations in: CO2 STD ±0.3, CO STD ±0.2, H2 STD ±0.2, CH4 STD ±0.07, H2S STD ±0.04, LHV.
Figure 1. Schematic drawing of the main components making up the entrained flow black liquor gasifier (courtesy of Chemrec)
Figure 2. Influence from assumed CO/CO₂ and fixed carbon ratio on CH₄ yield during pyrolysis. CH₄ yield defined as the mol fraction of methane released during pyrolysis relative 1 mol of carbon in dry black liquor. The CO/CO₂ ratio is constant along each line and marked with actual values in parentheses.
Figure 3. Profiles of CH₄ molar fraction vs. residence time at different temperatures in an isothermal plug flow reactor at 28 bar. Solid line: GRI-Mech. Dashed line: Jones and Lindstedt. The inlet molar gas composition was CH₄: 10%, CO₂: 20% CO: 20%, H₂O: 25%, H₂: 25%. The reactor temperatures were: 1273, 1400, and 1650 K for each respective case. Temperature is constant along each curve.
Figure 4. Profiles of $\text{H}_2$, $\text{H}_2\text{O}$, CO and CO$_2$ molar fraction vs. residence time (logarithmic scale) at different temperatures in an isothermal plug flow reactor at 28 bar. Solid line: GRI-Mech. Dotted line: Jones and Lindstedt. The inlet molar gas composition was CH$_4$: 10%, CO$_2$: 20%, CO: 20%, H$_2$O: 25%, H$_2$: 25%. The reactor temperatures were: 1273, 1400, and 1650 K for each respective case. Temperature is constant along each curve.
Figure 5. Numerical (obtained with CFD, empty circles) and experimental results (filled), units are % mol and MJ/kg (LHV, Lower heating value). Boundary conditions can be found in Tab. I.
Figure 6. Char conversion (left) and temperature (right) obtained from the CFD simulations.
Figure 7. Upper: Simulated CH₄ outlet concentration as function of simulated outlet temperature (left) and CH₄ as function of equivalence ratio (right) obtained from the simulations and from experiments (filled circles). Lower: Char conversion obtained from the simulation as function of outlet temperature (left) and equivalence ratio (right).