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Behavior of Black Liquor Nitrogen in
Combustion
– Formation of Cyanate

Niklas Vähä-Savo



Doctoral Thesis

Laboratory of Inorganic Chemistry

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Preface

This work was carried out at the Laboratory of Inorganic Chemistry at the Department of Chemical Engineering at Åbo Akademi University. This work is part of the activities of the Åbo Akademi Process Chemistry Centre. The Graduate School of Chemical Engineering funded a major part of this work, which made it possible to take part in courses and conferences abroad. In addition, part of this research work was funded by two projects: Chemcom 2.0 and Fusec, which are financed by the Finnish Funding Agency for Technology and Innovation (TEKES) and the companies Andritz Oy, Foster Wheeler Energia Oy, International Paper Inc., Metsä Botnia Ab, Clyde Bergemann GmbH, UPM-Kymmene Oyj, Top Analytica Oy Ab, and Valmet Power Oy. Financial support was also received from the Finnish Recovery Boiler Committee. All financial support is gratefully acknowledged.

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I am extremely grateful to Professor Mikko Hupa who gave me the opportunity to complete a M.Sc. thesis, and after that gave me the opportunity to continue with this work. He has motivated me during my work and his knowledge in the field of chemical recovery and thermal conversion of biomass and black liquor has been invaluable.

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I also wish to thank Per Tomani and Rufus Ziesig from Innventia AB, Hans Theliander from Chalmers University of Technology, and Erkki Välimäki from

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Special thanks to personnel at the UPM-Kymmene Kymi mill, particularly Toni Orava, for giving us the opportunity to conduct the measurement campaign published in Paper I. I also wish to thank KCL Kymen Laboratoriot Oy, especially M.Sc. Anja Hagman, for conducting the Kjeldahl nitrogen determinations for the samples used in this work. She also helped me a great deal to understand how the analysis is conducted so I could write about it in the experimental section.

During my doctoral studies, I had the great privilege to work with amazing colleagues at the Laboratory of Inorganic Chemistry, and I wish to thank you all. I particularly want to thank Luiz Bezerra for all the help he has given me with my experimental work and for all the good moments in the black liquor laboratory; it has been great to work with you. Also special thanks to my roommates Emil, Pati, and Rishabh. We have had interesting discussions about almost every possible topic during the past years. I also wish to thank Christoffer and Magnus for interesting discussions during the past years.

Finally, I would like to thank my parents, Annikki and Tapani, for their support during my doctoral studies, and my beautiful girlfriend Lumikki for the love and support she has given me, and for spell-checking part of this thesis.

Åbo, November 2014

Niklas Vähä-Savo

Abstract

The Kraft pulping process is the dominant chemical pulping process in the world. Roughly 195 million metric tons of black liquor are produced annually as a by-product from the Kraft pulping process. Black liquor consists of spent cooking chemicals and dissolved organics from the wood and can contain up to 0.15 wt% nitrogen on dry solids basis. The cooking chemicals from black liquor are recovered in a chemical recovery cycle. Water is evaporated in the first stage of the chemical recovery cycle, so the black liquor has a dry solids content of 65-85% prior to combustion. During combustion of black liquor, a portion of the black liquor nitrogen is volatilized, finally forming N_2 or NO. The rest of the nitrogen remains in the char as char nitrogen. During char conversion, fixed carbon is burned off leaving the pulping chemicals as smelt, and the char nitrogen forms mostly smelt nitrogen (cyanate, OCN^-). Smelt exits the recovery boiler and is dissolved in water. The cyanate from smelt decomposes in the presence of water, forming NH_3 , which causes nitrogen emissions from the rest of the chemical recovery cycle.

This thesis had two focuses: firstly, to determine how the nitrogen chemistry in the recovery boiler is affected by modification of black liquor; and secondly, to find out what causes cyanate formation during thermal conversion, and which parameters affect cyanate formation and decomposition during thermal conversion of black liquor.

The fate of added biosludge nitrogen in chemical recovery was determined in Paper I. The added biosludge increased the nitrogen content of black liquor. At the pulp mill, the added biosludge did not increase the NO formation in the recovery boiler, but instead increased the amount of cyanate in green liquor. The increased cyanate caused more NH_3 formation, which increased the NCG boiler's NO emissions. Laboratory-scale experiments showed an increase in both NO and cyanate formation after biosludge addition.

Black liquor can be modified, for example by addition of a solid biomass to increase the energy density of black liquor, or by separation of lignin from black liquor by precipitation. The precipitated lignin can be utilized in the production of green chemicals or as a fuel. In Papers II and III, laboratory-scale experiments were conducted to determine the impact of black liquor modification on NO and cyanate formation. Removal of lignin from black liquor reduced the nitrogen content of the black liquor. In most cases NO and cyanate formation decreased with increasing lignin removal; the exception was NO formation from lignin lean soda liquors. The addition of biomass to black liquor resulted in a higher nitrogen content fuel mixture, due to the higher nitrogen content of biomass compared to black liquor. More NO and cyanate were formed from the fuel mixtures than from pure black liquor. The increased amount of formed cyanate led to the hypothesis that black liquor is catalytically active and converts a portion of the nitrogen in the mixed fuel to cyanate.

The mechanism behind cyanate formation during thermal conversion of black liquor was not clear before this thesis. Paper IV studies the cyanate formation of alkali metal loaded fuels during gasification in a CO₂ atmosphere. The salts K₂CO₃, Na₂CO₃, and K₂SO₄ all promoted char nitrogen to cyanate conversion during gasification, while KCl and CaCO₃ did not. It is now assumed that cyanate is formed when alkali metal carbonate or an active intermediate of alkali metal carbonate (e.g. -CO₂K) reacts with the char nitrogen forming cyanate. By testing different fuels (bark, peat, and coal), each of which had a different form of organic nitrogen, it was concluded that the form of organic nitrogen in char also has an impact on cyanate formation.

Cyanate can be formed during pyrolysis of black liquor, but at temperatures 900°C or above, the formed cyanate will decompose. Cyanate formation in gasifying conditions with different levels of CO₂ in the atmosphere was also studied. Most of the char nitrogen was converted to cyanate during gasification at 800-900°C in 13-50% CO₂ in N₂, and only 5% of the initial fuel nitrogen was converted to NO during char conversion. The formed smelt cyanate was stable at 800°C 13% CO₂, while it decomposed at 900°C 13% CO₂. The cyanate

decomposition was faster at higher temperatures and in oxygen-containing atmospheres than in an inert atmosphere. The presence of CO₂ in oxygen-containing atmospheres slowed down the decomposition of cyanate.

This work will provide new information on how modification of black liquor affects the nitrogen chemistry during thermal conversion of black liquor and what causes cyanate formation during thermal conversion of black liquor. The formation and decomposition of cyanate was studied in order to provide new data, which would be useful in modeling of nitrogen chemistry in the recovery boiler.

Keywords: Black Liquor, Chemical Recovery, Combustion, Cyanate, Emissions, Gasification, Nitrogen, Pyrolysis, Recovery Boiler

Sammanfattning

Sulfatprocessen är den dominerande kemiska massaprocessen i världen. Ungefär 195 ton svartlut produceras årligen som biprodukt från sulfatprocessen. Svartlut består av förbrukade kokkemikalierna och från veden utlöst vedsubstans, samt kan innehålla upp till 0.15 vikt-% på torrvikts basis kväve. Kokkemikalierna från svartlutet återvinns i en kemikalieåtervinningscykel. Första skedet av kemikalieåtervinningen är indunstning av vatten, så att svartlutet får en torrhalt på 65-85% före det kan förbrännas i en sodapanna. Under förbränningen frigörs en del av kvävet i svartlutet som flyktiga kväveföreningar vilka slutligen bildar N_2 eller NO. Resten av kvävet blir kvar i kokset som koks kväve. Under koks förbränningen bränns det organiska materialet i kokset bort och kvar blir kokkemikalien i form av smälta. Största delen av koks kvävet omvandlas till smältkväve (cyanat, OCN^-) under koks förbränningen. Den kvarblivna smältan rinner ut ur sodapannan och löses upp i vatten. Cyanat i smältan sönderfaller i vattnet och bildar NH_3 , som orsakar kväveemissioner från resten av kemikalieåtervinningen.

Denna avhandling hade två mål. Första målet var att bestämma hur kvävekemin i sodapannan påverkas av modifiering av svartlut. Andra målet var att studera vad som orsakar cyanatbildning under termisk konversion och vilka parametrar som påverkar cyanatbildningen och sönderfallet under termisk konversion av svartlut.

Papper I handlar om ödet av tillsatta bioslammets kväve i kemikalieåtervinningen. Tillsatta bioslammet ökade svartlutets kvävehalt. Vid massafabriken, ökade det tillsatta bioslammet inte NO-emissionerna från sodapannan, men ökade istället mängden cyanat i grönlutet. Den ökade mängden cyanat höjde mängden NH_3 som bildas, vilket i sin tur ökade NO-emissionerna från anläggningen som förbränner de icke-kondenserbara gaserna. Laboratorieskala experiment visade att både NO- och cyanatbildningen ökade efter bioslamtillsättningen.

Svartlut kan modifieras t.ex. genom att tillsätta fast biomassa i det för att öka dess energi täthet eller genom att separera lignin från svartlut. Det separerade ligninet kan användas för produktion av kemikalier eller som bränsle. I Papper II och Papper III utfördes experiment i laboratorieskala för att bestämma hur modifiering av svartlut påverkar NO- och cyanatbildningen. Separering av lignin minskade svartlutets kvävehalt. I de flesta fall minskade både NO- och cyanatbildningen med ökande ligninborttagning, enda undantaget var NO-bildningen från det ligninfattiga sodalutet. Tillsats av biomassa i svartlut ökade bränsleblandningens kvävehalt, för biomassan hade högre kvävehalt än svartlutet. Mera NO och cyanat bildades från bränsleblandningarna än från rent svartlut. Den ökade mängden bildat cyanat resulterade i hypotesen att svartlut är katalytiskt aktivt och omvandlar en del av kvävet i det blandade bränslet till cyanat.

Mekanismerna bakom cyanatbildningen under termisk konversion av svartlut var inte klara före denna avhandling. Papper IV studerar cyanatbildning under gasifiering i CO₂ innehållande gassammansättning av bränslen laddade med olika alkalimetallsalter. Salterna K₂CO₃, Na₂CO₃, och K₂SO₄ gynnade omvandling av kokskväve till cyanat, medan KCl och CaCO₃ inte gynnade. Det antas nu, att cyanat bildas när alkalimetallkarbonat eller en aktiv intermediär av alkalimetallkarbonat (-CO₂K) reagerar med kokskväve och bildar cyanat. Bränslets ålder påverkar hur det organiska kvävet är bundet. Genom att testa olika bränslen av olika ålder (bark, kol, och torv) kunde man dra slutsatsen att formen av organiskt kväve i kokset påverkar cyanatbildningen.

Cyanat kan bildas under pyrolys av svartlut, men i temperaturer över 800°C sönderfaller cyanat snabbt. Cyanatbildningen under gasifiering i olika mängder CO₂ i atmosfären studerades också. Största delen av kokskvävet bildade cyanat under gasifiering i 800-900°C i 13-50% CO₂ (som balans användes N₂) atmosfär och under 5% av svartlutets kväve bildade NO. Cyanat i smältan var stabilt i 800°C vid 13% CO₂ medan det skedde sönderfall i 900°C vid 13% CO₂. Cyanatsönderfallet var snabbare i högre temperaturer och syreinhållande

atmosfär än i inert atmosfär. Närvaro av CO₂ i syreinhållande atmosfär bromsade ned sönderfallet av cyanat.

Detta arbete för fram ny information om hur modifiering av svartlut påverkar kvävekemin under termisk konversion av svartlut och vad som orsakar cyanatbildningen under termisk konversion av svartlut. Bildning och sönderfall av cyanat studerades för att få ny data vilket skulle vara användbart i modellering av kvävekemin i en sodapanna.

Nyckelord: Cyanat, Emission, Förbränning, Gasifiering, Kemikalieåtervinning, Kväve, Pyrolys, Sodapanna, Svartlut

Publications

List of publications included in this thesis:

- I. Vähä-Savo, Niklas; DeMartini, Nikolai; Hupa, Mikko. *Fate of biosludge nitrogen in black liquor evaporation and combustion* Tappi Journal (2012), 11(9), 53-59
- II. Vähä-Savo, Niklas; DeMartini, Nikolai; Ziesig, Rufus; Tomani, Per; Theliander, Hans; Välimäki, Erkki; Hupa, Mikko. *Combustion Properties of Reduced Lignin Black Liquors* Tappi Journal (2014), 13(8), 81-90
- III. Vähä-Savo, Niklas; DeMartini, Nikolai; Hupa, Mikko. *Combustion of Black Liquor-Solid Biomass Mixtures in a Single Particle Reactor-Characteristics and Fate of Nitrogen* Energy & Fuels (2011), 25(11), 4944-4951
- IV. Vähä-Savo, Niklas; DeMartini, Nikolai; Hupa, Mikko. *Fate of Char Nitrogen in Catalytic Gasification – Formation of Alkali Cyanate* Energy & Fuels (2013), 27(11), 7108-7114
- V. Vähä-Savo, Niklas; DeMartini, Nikolai; Engblom, Markus; Brink, Anders; Hupa, Mikko. *The Fate of Char Nitrogen in Black Liquor Combustion - Cyanate Formation and Decomposition* submitted to Industrial & Engineering Chemistry Research

Author contributions

Papers I-IV. Niklas Vähä-Savo was the main author in these papers. The experimental matrix in these papers was planned by Niklas Vähä-Savo, Nikolai DeMartini, and Mikko Hupa. All the experimental work was carried out by the main author with the help of Luis Bezerra, except for the Kjeldahl Nitrogen determinations, which were conducted at KCL Kymen Laboratoriot Oy.

Paper II. Rufus Ziesig helped with the writing of Innventia AB's lignin removal process. He, Per Tomani, Hans Theliander, and Erkki Välimäki were also involved in planning of the experimental matrix in this work.

Paper V. Anders Brink and Markus Engblom were involved in planning of the experimental work, gave comments on the results, and helped to finalize the paper.

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1 INTRODUCTION

In 2012, more than 130 million metric tons of chemical pulp was produced, of which more than 95% originated from the Kraft pulping process [1]. For every metric ton of Kraft pulp produced, roughly 10 metric tons of weak black liquor or about 1.5 metric tons of black liquor solids is produced as a side product [2]. Black liquor is combusted in a recovery boiler, thus making it the fifth-most important fuel in the world [3]. In Finland in 2011, roughly 29% of the energy consumed originated from renewable energy sources: biomass; hydro, wind, and solar power; and heat pumps. The distribution of renewable energy sources in Finland in 2011 is shown in Figure 1. In Finland, one-third of the renewable energy originates from the combustion of black liquor.

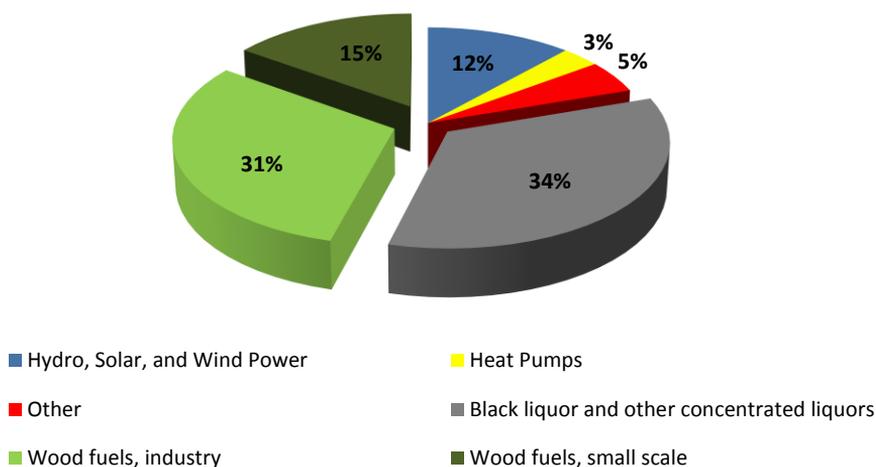


Figure 1. Renewable energy sources in Finland in 2011 [4].

1.1 Overview of Kraft pulping and chemical recovery

In the Kraft pulping process, fibers are separated from wood by delignification of the wood using an aqueous solution of Na_2S and NaOH in a digester at temperatures of approximately 160-175°C. After pulping, two streams are

separated from the digester: the main product pulp, which is used in paper making, and the by-product black liquor, which contains the spent cooking chemicals and dissolved organic compounds from the wood [5]. The spent cooking liquor is recycled in the Kraft recovery cycle [2]. A schematic overview of the chemical recovery cycle is shown in Figure 2. After digestion, black liquor has a dry solids content of approximately 15%, and it is concentrated in the evaporators prior to combustion in a recovery boiler. During evaporation, water is removed from black liquor. When the dry solids content of black liquor is above 65%, it is combusted in the recovery boiler. The recovery boiler has dual purposes: to recover the inorganic cooking chemicals and to produce steam and electricity needed in the pulp mill.

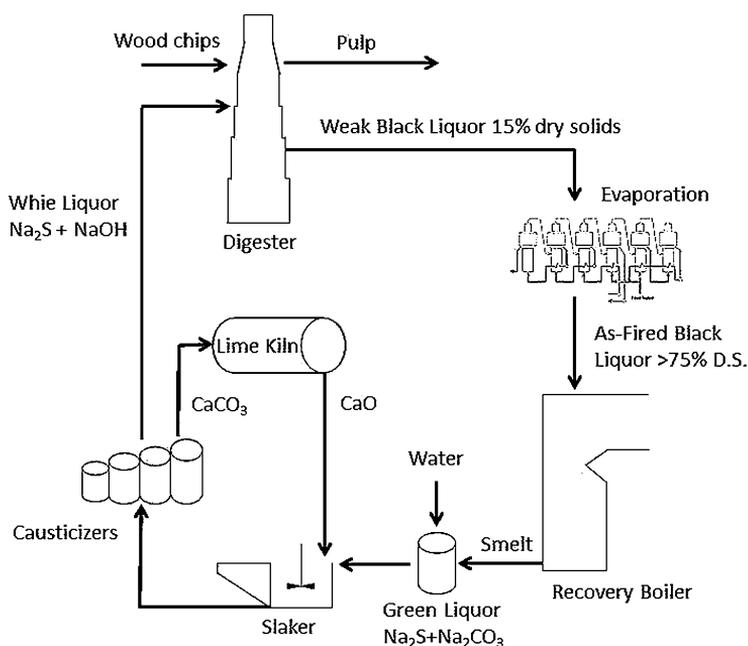


Figure 2. Overview of the chemical recovery cycle.

After the organic material from the black liquor is combusted, an inorganic smelt remains. The smelt runs through a smelt spout out from the recovery boiler to a smelt dissolving tank, where it is dissolved in water. At this point the smelt is called green liquor. The next step is the causticizing process, in which calcium

oxide is mixed with the green liquor in order to convert the sodium carbonate in the green liquor to sodium hydroxide. When the sodium carbonate is converted to sodium hydroxide the liquor is called white liquor, which can then be reused in the pulping. During causticizing, the calcium oxide is converted to calcium carbonate, which is separated from the liquid phase and heated to 1000°C in a lime kiln to volatilize CO₂ from the calcium carbonate and obtain calcium oxide.

1.2 Black liquor combustion

When black liquor is sprayed into the recovery boiler it forms a sheet, which breaks down to black liquor droplets with varying diameters, Figure 3. The combustion of a black liquor droplet is divided into three separate stages: drying, devolatilization, and char burning [6], as shown in Figure 4. In the first phase, the temperature inside the black liquor droplets increases to above 100°C and the water in black liquor is evaporated.

During devolatilization, light organic compounds are formed and volatilized from the black liquor droplet. The volatiles react with oxygen and are burned with a visible flame around the droplet. In the recovery boiler, the final oxidation of the volatile compounds occurs with the combustion air from the tertiary air level. Unlike other char-forming fuels, the black liquor droplet swells considerably during the devolatilization phase due to the release of the volatile compounds. The degree of swelling depends on the liquor, temperature, and atmosphere [6-9]. Some of the swollen droplets can be entrained in the flue gas flow forming so-called carry-over particles, which can form deposits in the upper furnace [10].

When all the volatile matter is released from the swollen particle, the visible flame disappears and a heavily-swollen porous char remains. During char burning, the size of the char decreases as the remaining organic matter reacts with oxygen, water, and CO₂, and finally an inorganic smelt remains [6].

The char can form a char bed in the lower furnace of the recovery boiler. Combustion air from primary and secondary air ports supplies oxygen to the surface of the char bed to oxidize the organic material in the char so that a smelt is formed. The smelt consists of Na_2CO_3 , Na_2S , and Na_2SO_4 . The carbon remaining in the char bed reduces sulfate in the smelt to sulfide as the smelt flows through the char bed. The smelt exiting the recovery boiler consists mostly of sodium sulfide and sodium carbonate.

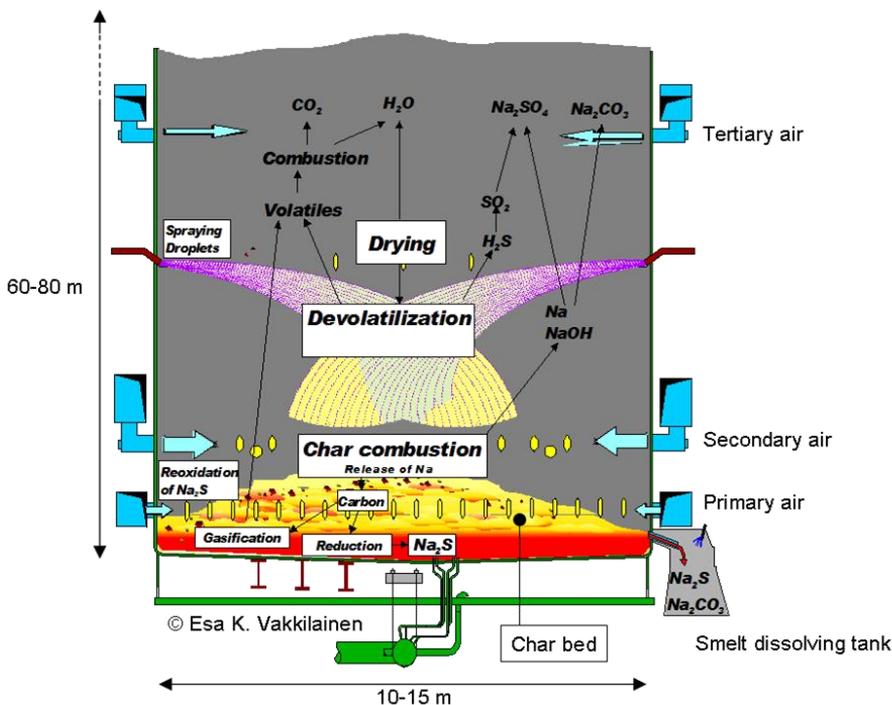


Figure 3. A schematic picture of black liquor spraying into a recovery boiler furnace [11].

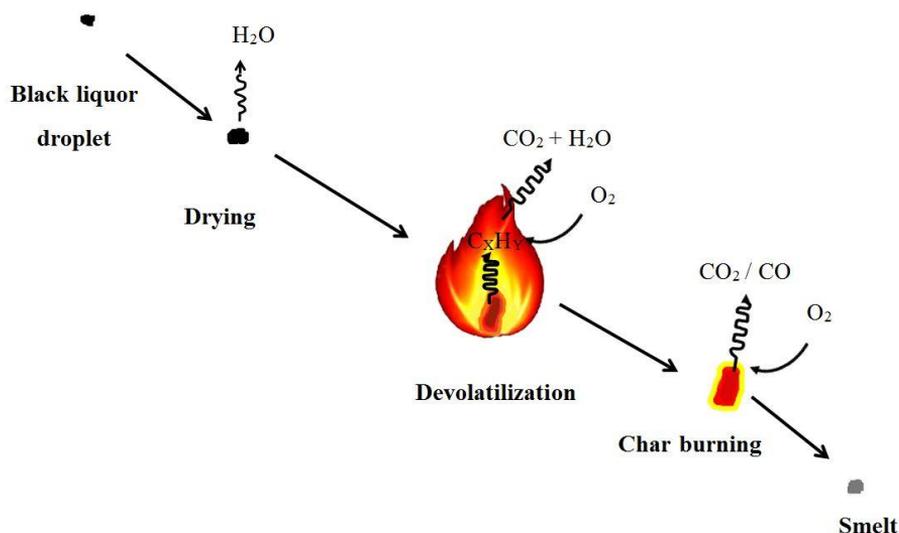


Figure 4. Stages in black liquor droplet combustion.

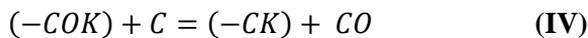
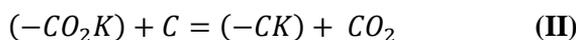
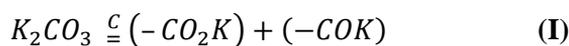
1.3 Black liquor gasification

An alternative method for recovering the inorganics and utilizing the organics in the black liquor is gasification. In black liquor gasification, the organic material is transformed mainly to CO and H₂ gases in oxygen-lean conditions. The formed gases are called syngas, which can e.g. be catalytically converted to methane or dimethyl ether [12, 13]. At the moment there are no operational full-scale black liquor gasification plants; however, a few existing demo- and pilot-scale plants were used earlier to study the gasification of black liquor. Also, the catalytic upgrade of syngas from black liquor gasification to methanol and dimethyl ether has been extensively studied [14, 15].

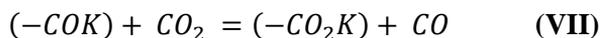
Black liquor contains roughly 20-25 wt% alkali metals, which are active catalysts in gasification [16-21]. Due to the high alkali metal content, black liquor has also been studied as a cheap source of alkali metal catalyst in co-gasification with cutter dust [22], sawdust [23], and petroleum coke [24]. Several mechanisms for gasification of fuels containing high levels of alkali metals have been proposed [25]. It has been suggested that the alkali metal either

forms a reactive metal or metal oxide [26-28]. Sams and Shadman [29] proposed a reaction mechanism for potassium carbonate catalyst on a carbon surface: The reaction mechanism is separated into reduction of the catalyst with char carbon and oxidation of the catalyst with CO₂. The first step is that K₂CO₃ forms a fully (-CO₂K) or a partially oxidized (-COK) form on the carbon surface (I). These two formed potassium compounds react with the carbon forming CO or CO₂ (II-IV). Finally the reduced potassium (-CK) can be either released as K_(v) (V) or be oxidized with CO₂ back to partially oxidized form which can be further oxidized to a fully oxidized form (VI-VII).

Reduction of the catalyst:



Oxidation of the catalyst:



This proposed mechanism is later used in section 4.3.2 to describe the possible mechanisms behind cyanate formation during catalytic gasification. Similar mechanisms have been used to describe the role of alkali metal carbonates in black liquor gasification [30, 31].

1.4 Nitrogen emissions from pulp mills

Black liquor originates from biomass and is considered a CO₂-neutral fuel. The nitrogen, sulfur, and dust emissions for the pulp mills are restricted by the European Commission Integrated Pollution Prevention and Control (IPPC) document for best available technology (BAT), Table I [32]. The emissions formed from combustion of debarking residues are not included in the pulp mill emissions limit shown in Table I. The limits are quantified as kg of formed emission per one metric ton of air-dried pulp produced. The emission limits consist of combustion of black liquor in the recovery boiler, and the emissions formed from the lime kiln and the non-condensable gas boiler (NCG boiler), where low-volume high-concentrated gases collected mainly from the digester and evaporation are incinerated.

Table I. Emission limits for Kraft pulping [32].

| | Dust kg/Adt | SO ₂ (as S) kg/Adt | NO _x (NO+NO ₂ as NO ₂) kg/Adt | TRS (as S) kg/Adt |
|------------------------------------|----------------|----------------------------------|--|----------------------|
| Bleached and unbleached Kraft pulp | 0.2-0.5 | 0.2-0.4 | 1.0-1.5 | 0.1-.02 |

There are three major NO_x emission sources in the pulp mill: combustion of black liquor in the recovery boiler; combustion of oil, natural gas, and wood powder in the lime kiln; and incineration of NCG gases and methanol in the NCG boiler or lime kiln [33]. The other source of nitrogen emission, which is not regulated, is ammonia (NH₃). Ammonia originates from the wood proteins and amino acids. Some ammonia is formed during pulping. The rest is formed from smelt nitrogen in the recausticizing process. The form of nitrogen in smelt is cyanate. The ammonia in weak black liquor is volatilized in the early stages of black liquor evaporation and is collected in the methanol and NCG's. The ammonia formed during smelt dissolution and recausticizing is released in the smelt dissolver, during green liquor handling, and white liquor preparation while a part of it returns to the digester with the white liquor [34]. If the formed

ammonia is collected and incinerated in the NCG boiler or in the lime kiln, it may contribute to the pulp mill's NO_x emissions.

1.5 Purpose of this work

The main objectives of this thesis were to:

- Determine the impact of black liquor modification on the NO and cyanate formation during thermal conversion of black liquor.
- Shed light on cyanate formation during thermal conversion of black liquor by studying cyanate formation during gasification of alkali metal salt loaded fuels.
- Study the parameters affecting cyanate formation and decomposition during thermal conversion of black liquor. This work would provide data for modeling the fate of black liquor nitrogen in the recovery boiler.

During the NO formation experiments, the combustion characteristics of the modified black liquor were obtained. The combustion characteristics of modified black liquors are discussed in detail in **Papers I-III**.

The main task of **Paper I** was to determine the fate of biosludge nitrogen in the chemical recovery cycle, as this issue remained partially unclear after a previous mill sampling campaign [35].

The growing interest in increasing the profitability of chemical pulping has resulted in the identification of different scenarios of how pulp mills could be more profitable. One possible scenario is the production of green chemicals and fuels from wood. Utilization of lignin, which can be separated from black liquor, is one possible source for production of chemicals. Other possible options to increase pulp mill profitability include an increase in the power production of stand-alone pulp mills that have condensing turbines with surplus recovery boiler capacity by co-firing black liquor with other biomass-based fuels. The impact of these black liquor modifications on the combustion properties, NO formation, and cyanate formation was studied in **Paper II** and **Paper III**.

The main objective of **Paper IV** was to gain a better understanding of the reason cyanate is formed in black liquor conversion. Only a few studies have been conducted in order to determine what causes cyanate formation. Kymäläinen et al. [36] suggested that cyanate formation is caused by the alkali metals in black liquor, and later Forssén et al. [37] studied the forms of char nitrogen in black liquor chars and their potential impact on cyanate formation. Before this thesis work, the mechanisms behind cyanate formation were unknown. **In Paper IV** the cyanate formation was studied by gasifying different fuels loaded with different alkali metal salts.

The first objective of **Paper V** was to determine the cyanate formation during pyrolysis of black liquor and gasification of black liquor chars in CO₂-containing atmospheres at different temperatures. The second objective was to obtain data regarding the decomposition of cyanate in smelt droplets, which will clarify the parameters affecting cyanate decomposition in smelt. The amount of formed NO was measured during the cyanate formation and decomposition experiments. This work would provide data for more accurately modeling the fate of black liquor nitrogen in a Kraft recovery boiler.

2 LITERATURE REVIEW

2.1 Nitrogen

2.1.1 Nitrogen in fuels of different maturity

The form of nitrogen-containing organic compounds in a fuel depends largely on the maturity of the fuel. The youngest type of fuel used in power generation is biomass. In biomass, the organic nitrogen is mainly found in free or protein-bound amino acids [38-41]. In peat, which is biomass that has partially decayed, the organic nitrogen is mainly in the form of amide and amino acid structures, and to a lesser extent in pyrrole and pyridine structures [42-44]. Over many years, peat is slowly converted to coal and the form of the nitrogen-containing structures changes. In coals the organic nitrogen is found mainly in heterocyclic compounds (pyridine, pyrroles, imidazoles, and indoles) [45, 46]. Structures of different nitrogen-containing organic compounds are shown in Figure 5.

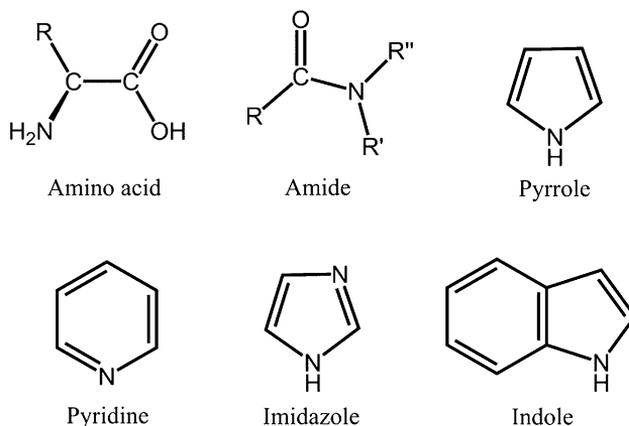


Figure 5. Different organic nitrogen compounds found in fuels of different maturity.

2.1.2 Nitrogen during thermal conversion of solid biomass or fossil fuel

During thermal conversion of biomass or fossil fuel, the fuel-bound nitrogen is either released as volatile nitrogen or remains in the char as char nitrogen. The volatile nitrogen can be further divided into low molecular gaseous nitrogen compounds and tar nitrogen, which consists of one- and two-ring structures containing nitrogen [47-49]. At temperatures above 600°C, the coal tars decompose to form the low molecular gaseous nitrogen compounds HCN, NH₃, and HNCO [50]. The share of volatile nitrogen and the ratio between NH₃/HCN depends on the fuel type, temperature, and heating rate of the fuel [47, 51-54]. The volatile yield is higher for biomass than for fossil fuels. More of the nitrogen in biomass is volatilized as NH₃ than as HCN, while it is the opposite for nitrogen volatilized from fossil fuels [51, 54].

During gasification in CO₂, H₂O, or a low oxygen containing atmosphere, char nitrogen can be converted to gaseous nitrogen species [55, 56]. During combustion, the volatile nitrogen and char nitrogen can be oxidized to form NO and NO₂ or reduced to form N₂ [54, 57]; small amounts of N₂O can also be formed during combustion [58]. In addition to fuel nitrogen, nitrogen in the surrounding atmosphere can also contribute to NO_x formation. At elevated temperatures (>1500°C), thermal NO_x can be formed when nitrogen in the combustion air reacts with oxygen-containing radicals [59]. Hydrocarbon radicals formed during combustion can react with nitrogen, forming so-called prompt NO_x [60]. A simplified picture of fuel nitrogen during thermal conversion, based on the literature described above, is shown in Figure 6.

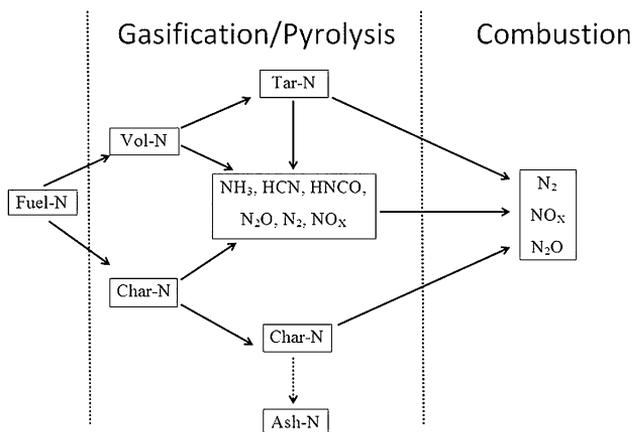


Figure 6. Fate of fuel nitrogen during thermal conversion processes.

2.1.3 Nitrogen in black liquor

Black liquor has a nitrogen content of 0.06-0.15 wt% dry solids basis, which depends mainly on the wood type used in pulping. The nitrogen content of black liquor originating from hardwood pulping is on average slightly higher than softwood black liquor's nitrogen content [61, 62]. The nitrogen in black liquor originates mainly from protein amino acids dissolved from wood during pulping [63]. The form of nitrogen in black liquor has not been well-studied; in one study, roughly 80% of the black liquor nitrogen compounds could not be determined due to detection limits in the analysis methods used [64]. The 20% of black liquor nitrogen compounds that were identified were either in five- and six-membered ring structures (pyrroles, pyridines, and indoles) or in straight chain amino acids (aspartic acid, cysteine, glutamic acid, leucine, proline, and valine), and the rest is assumed to be in organic form [64, 65]. The major component of the dissolved organics in black liquor is lignin. A study by Dill et al. [66] showed that nitrogen in lignin is exclusively in amino acid form, and that at least 50% of the total nitrogen in wood was found in the lignin fraction. Martin et al. [64] showed that most of the black liquor nitrogen was found in lignin from the acid-precipitation. Analytical results for several black liquors were reported by DeMartini et al. [67]. It was reported that 5-15% of the

nitrogen in weak black liquor was in the form of ammonia, 15% was bound to lignin, 10-15% was amino acids, 2-5% in heterocyclic compounds, and 40-50% in other nitrogen containing compounds. The ammonia in the weak black liquor originated partly from the decomposition of amino acid and protein during pulping and partly from the white liquor. The unidentified nitrogen compounds were speculated to be protein fragments, which were not detectable by high-performance liquid chromatography.

2.1.4 Nitrogen during thermal conversion of black liquor

The fate of black liquor nitrogen in a recovery boiler is shown in Figure 7. During thermal conversion of black liquor, the fuel bound nitrogen is either released during pyrolysis or remains in the char. Aho et al. [61] showed that in laboratory conditions, between 20 and 60% of black liquor nitrogen is released during pyrolysis, mainly as NH_3 and N_2 . Some NO was also detected, but no HCN was detected [61, 68]. In full-scale recovery boiler measurements, small amounts of HCN have been measured [69]. It is believed that HCN originates from the reaction between NO and hydrocarbons formed during devolatilization. Laboratory-scale black liquor combustion tests showed that around 60% of the black liquor nitrogen is released during devolatilization and the rest during char oxidation [62, 70]. In recovery boilers the volatile nitrogen compounds are oxidized to form primarily NO or reduced to N_2 .

After all the volatile matter is released, a swollen char remains. During char burning, the size of the char decreases as the remaining organic matter reacts with oxygen and oxygen containing compounds. Forssén et al. [71] studied the NO formation during black liquor char oxidation and gasification and came to the conclusion that during slow oxidation and gasification of black liquor, char nitrogen will remain in the smelt and will be released if the smelt is oxidized. Later Kymäläinen et al. [72] identified the smelt nitrogen to be cyanate, and also confirmed the work by Forssén et al. [71], that most of the char nitrogen remains in the smelt [36]. In recovery boilers, 35% or less of the black liquor nitrogen

remains in the smelt and exits the boiler; under 35% forms NO; and the rest forms N₂ [35, 73].

In recovery boilers, a portion of the black liquor droplets form carry-over particles, which follow the flue gas flow and can form deposits. This means that a portion of the black liquor nitrogen can thus end up in the upper furnace.

Researchers generally believe that thermal NO_x is not formed during black liquor combustion because the temperatures inside the recovery boiler furnace are below 1500°C [74-76].

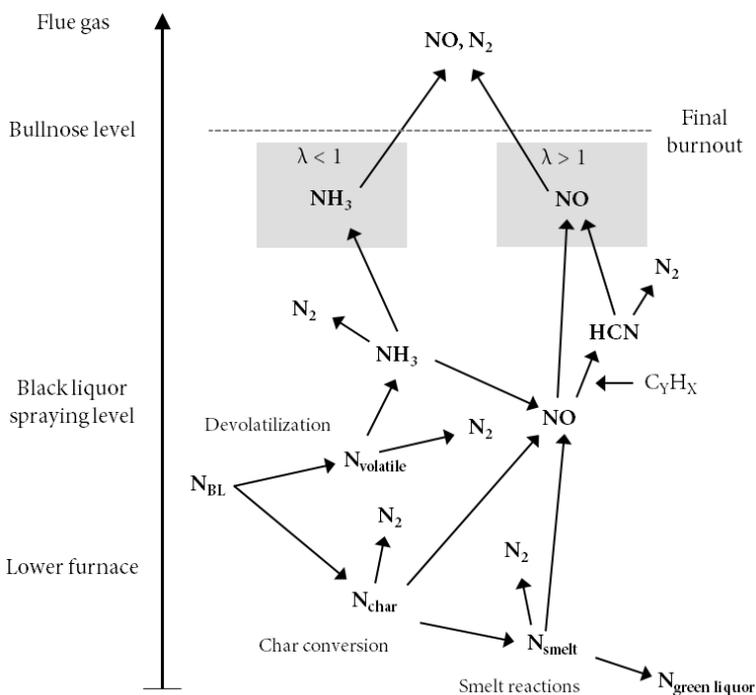


Figure 7. Main black liquor nitrogen pathways in recovery boiler [77].

2.1.5 Nitrogen in the chemical recovery cycle

Nitrogen entering the chemical recovery cycle originates mainly from the wood that is pulped. Wood is digested with white liquor, forming pulp and black

liquor. Wood contains roughly 0.05-0.25 wt% nitrogen, depending on the wood species [63], and white liquor contains 54-83 mg nitrogen/L and is mainly in the form of ammonia [35]. Most of the nitrogen exits the digester with the weak black liquor, and the rest with the pulp or as gaseous nitrogen compounds formed during pulping [35, 67, 78]. After the digester, the pulp is transported to brownstock washing where cooking chemical residues are washed from the pulp. The nitrogen in the pulp returns with the washing liquor, which is mixed with weak black liquor. Figure 8 shows the nitrogen distribution around pulping in three Kraft pulp mills.

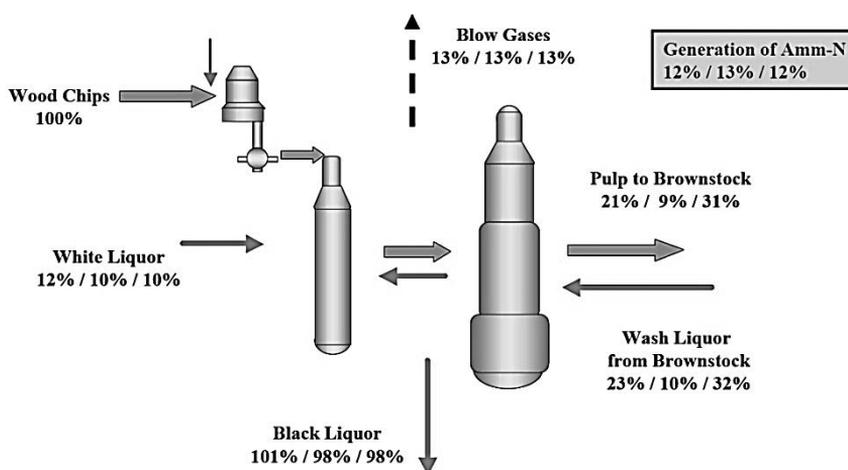


Figure 8. Nitrogen distribution around pulping in three Kraft pulp mills [67].

After the digester, weak black liquor enters the chemical recovery cycle. In the first step of chemical recovery, the water from the weak black liquor is evaporated. In the early stages of evaporation, nitrogen is volatilized as NH_3 and other volatile nitrogen species, ending up in methanol and non-condensable gases [35, 67, 78, 79]. After the initial nitrogen removal, the nitrogen content in the black liquor remains constant during the rest of evaporation [67].

When the black liquor reaches dry solids content exceeding 65%, it is combusted in a recovery boiler. Roughly 60-70% of the black liquor nitrogen is volatilized in the recovery boiler and forms N_2 or NO , and the rest of the black liquor

nitrogen remains in the char [62, 70, 73]. During slow char oxidation and/or gasification to smelt, most of the char nitrogen is converted to cyanate [36, 71]. The formed smelt nitrogen (cyanate) can decompose thermally to form N_2 or oxidize to form NO, but less than 35% of the black liquor nitrogen exits the recovery boiler with the smelt [70, 78, 80].

The smelt runs out of the recovery boiler to a smelt dissolver where it is mixed with weak wash or water to form green liquor. The distinct smell of ammonia has been noted around the smelt dissolver [81], and Kymäläinen et al. [72] confirmed that cyanate decomposes in the presence of water, forming ammonia. The rate of ammonia formation is affected by temperature, pH and carbonate content of the green liquor [82, 83]. Previous studies have shown that it takes up to 44 hours at 90°C for 90% of the smelt nitrogen to be converted to ammonia [72]. Thus, ammonia is formed in the dissolving tank and in the green liquor tank, during green liquor clarification, slaking, causticizing, and in the white liquor tank. A portion of the ammonia is released from the system while the rest remains in the liquid phase and reenters the digester with the white liquor [67, 70, 78]. A general overview of the nitrogen in the chemical recovery cycle is shown in Figure 9.

The cyanate formation and decomposition plays an important role in the pulp mill's overall nitrogen emissions. A better understanding of the mechanics and kinetics of cyanate formation and decomposition could be utilized to minimize cyanate formation to lower the overall nitrogen emissions of the pulp mill.

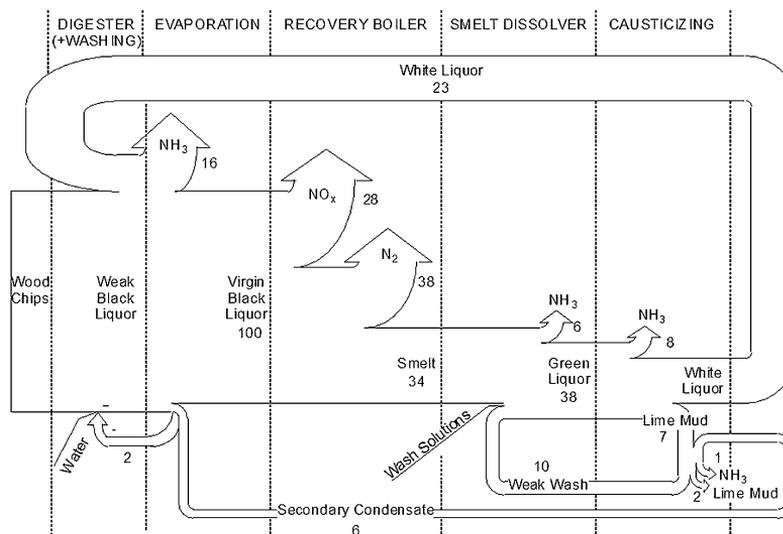


Figure 9. Overview of nitrogen flows in the chemical recovery cycle [78].

2.2 Modification of black liquor

2.2.1 Biosludge addition to black liquor

Biosludge consists of sludge from mechanical waste water clarification and microbial biomass from biological waste water treatment [84]. Biosludge can be disposed of by mixing it with debarking residue or black liquor and incinerating the mixture in a biomass boiler or recovery boiler [84-86]. Even a small addition of biosludge to black liquor can increase the nitrogen content of the black liquor by about 30% [35, 86]. In the work by Kymäläinen et al. [35], roughly 10% of the nitrogen content in added biosludge was ammonia, which was expected to be volatilized during evaporation. The addition of biosludge did not increase the NO formation at the recovery boiler or the amount of cyanate in the green liquors. The fate of biosludge nitrogen remained unclear.

2.2.2 Biomass addition to black liquor

In stand-alone pulp mills that have a modern Kraft recovery boiler with condensing turbines, the pulp mill's energy needs are fully met by the recovery boiler. In these pulp mills, no biomass boiler is needed and the residue from debarking can be used to improve the soil quality or sold to a power boiler owner for power production [87]. During periods of low pulp production, or when the recovery boiler has excess capacity, the electricity production of the recovery boiler can be increased by co-firing biomass with black liquor. Biomass residue from pulping (wood and bark) has a Higher Heating Value (HHV) of 17-21 MJ/kg dry solids basis (dsb) [88, 89] while black liquor has a considerably lower HHV, 13-15 MJ/kg dsb [21]. This means that a 90% black liquor 10% biomass residue fuel mixture would have a roughly 5% higher HHV than pure black liquor, which would ultimately increase the heat formation in the recovery boiler.

2.2.3 Lignin removal

Roughly seven decades ago, Tomlinson, G.H. and Tomlinson, G.H. Jr. presented the idea of separating lignin from spent pulping liquors by lowering the pH of the spent liquor to 8.5 with flue gas containing CO₂ [90]. By lowering the spent cooking liquor pH to 8 with CO₂, almost 80% of the lignin can be precipitated from the spent cooking liquor [91]. The dry solids content of the spent cooking liquors prior to acidification plays an important role in the lignin precipitation yield. For Kraft or soda liquors from pine pulping, the maximum precipitation yield is obtained at a dry solids content of 27-30%, whereas for birch liquors the maximum precipitation yield is obtained at 30-35% dry solids [92]. The separated lignin can be utilized in various applications in the chemical industry or as fuel, which has led to increased interest in large-scale lignin separation [93-95]. One such separation process is the LignoBoost process, Figure 10. A stream of black liquor from the storage tank is cooled and mixed with gaseous CO₂ to precipitate the dissolved lignin. The precipitated lignin is separated with a filter

The separated lignin has a HHV around 23-27 MJ/kg dsb [97], which is considerably higher than the HHV of black liquor. Due to its high HHV, the separated lignin can be used in the pulp mill to replace fossil fuels, for example in the lime kiln [100, 101]. Lignin removal will significantly decrease the HHV of Kraft black liquor. Based on the changes in black liquor composition with different levels of lignin separation, lignin removal up to an estimated 20% is possible without any considerable changes in the recovery boiler operations; at 40-50% lignin removal, the recovery boiler can still operate without support fuel [98, 102].

Removal of lignin is also an alternative to increase pulp production if the mill is recovery boiler-limited. Lignin extraction from weak black liquor means that less as-fired black liquor is produced per ton of pulp, thus decreasing the recovery boiler load, which creates the possibility to increase pulp production [103].

3 METHODS AND MATERIALS

3.1 Methods

3.1.1 Single particle reactor

The combustion characterization and the cyanate formation and decomposition experiments were conducted in a single particle reactor. The single particle reactor is constructed of quartz glass, and the reactor can be heated up to 1100°C. A schematic drawing of the single particle reactor is shown in Figure 11. The total gas flow through the reactor was 220 NL/h and the gas composition can be adjusted. Roughly 40 NL/h of the gas flow was routed through the sides of the reactor and through the sample insertion mantel. The rest of the gas flow entered the reactor from the bottom. N₂ was used as background gas because air was used as the source of oxygen in the combustion experiments. 20 NL/h of pure N₂ flowed through the sample insertion mantel in order to prevent the sample from reacting before inserting it to the reactor, and also to quench reactions at the end of an experiment. The gases flowing out of the top of the reactor can be directed to an online gas analyzer. In the combustion experiments and selected cyanate experiments, the NO emissions were measured with a chemiluminescence analyzer (Teledyne model 200EM). In the combustion experiments, six droplets of each sample were combusted to obtain a reliable average and standard deviation for the NO formation.

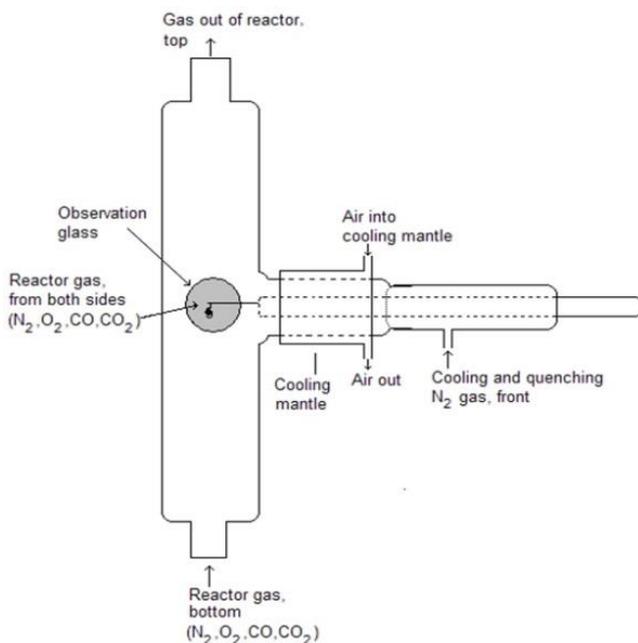


Figure 11. Schematic drawing of the single particle reactor [104].

The combustion experiments can be recorded from the side of the reactor. The recorded digital video was used to determine combustion times and maximum swollen volume of the samples. Devolatilization time was estimated from the appearance of the flame around the black liquor droplet to the point at which the flame disappears. Char burning time was determined from the disappearance of the flame to the point where smelt coalescence occurs. The maximum swollen volume of a droplet was determined by capturing an image from the recorded video, Figure 12. The captured image was converted to black and white, where the droplet is black and the background is white. A circle or an ellipse (with the same area of the pixels as the swollen particle) was fitted to the swollen particle in the two-dimensional image. The volume of a corresponding sphere or ellipsoid was calculated to obtain a rough estimate of the maximum swollen volume. The maximum swollen volume was then normalized to droplet dry solids weight.

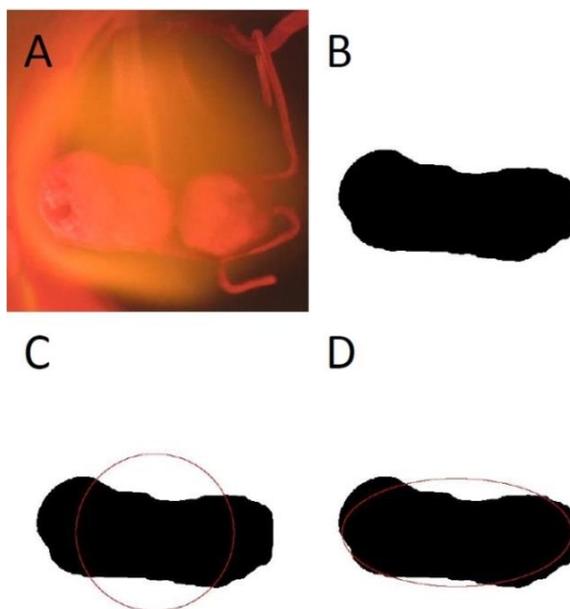


Figure 12. Determination of maximum swollen volume. A, Captured image B, black and white image of the droplet based on image A. Fitted circle C, and ellipse D.

The combustion experiments were conducted mainly in 10% O₂ in N₂ at 900°C because at these conditions the appearance and disappearance of the flame is clear. In some experiments higher temperature and lower oxygen concentrations were used as these conditions are closer to modern recovery boiler conditions.

Kymäläinen et al. [36] performed the first smelt nitrogen (cyanate) formation experiments more than 10 years ago. In her work the samples were first pyrolyzed in 100% N₂ to form chars followed by gasification of the chars in 13% CO₂/87% N₂. Her work also concluded that cyanate was stable in 13% CO₂/87% N₂ at temperatures below 850°C. Based on her work, the cyanate formation experiments in this thesis were mainly conducted at 800°C and according to her procedure: pyrolysis followed by gasification of the char.

3.1.2 Nitrogen analysis

3.1.2.1 Modified Kjeldahl method

The modified Kjeldahl analysis for the determination of total nitrogen was conducted at KCL Kymen Laboratoriot Oy based on the SFS5505:1988 standard method. The sample (<0.5 g dry solids basis of solid sample or 4-5 ml wet black liquor) was mixed with ultrapure water so that the total volume of sample and water was 50 ml. To the sample water mixture, 5 ml of concentrated H₂SO₄, one Kjeltabs Cu-3.5 (3.5 g K₂SO₄ + 0.4 g CuSO₄·5H₂O), and a small amount of Devarda's alloy was added. Kjeltabs catalyzes the decomposition of the sample. The mixture was heated over a period of two hours to 200-240°C, after which it was slowly heated to 365°C. The mixture was digested at 365°C for four hours. During digestion, most of the nitrogen in the sample is converted to ammonium sulfate (NH₄)₂SO₄. The Devarda's alloy reduces the liberated nitrate and nitrite to ammonia. After digestion, the mixture is cooled down and a 40% NaOH and water solution is added to it. The added NaOH reacts with ammonium (NH₄⁺), converting it to ammonia (NH₃). The mixture containing the sample is then steam distilled, and the liberated ammonia is captured in a 1% boric acid solution containing a mixture of Bromocresol green and methyl red indicators. The color of the boric acid solution changes when ammonia is captured. After all of the ammonia was captured, the boric acid is then titrated with a 0.01N H₂SO₄ solution and the reverse color change is recorded. The amount of nitrogen is then calculated based on the amount of H₂SO₄ used during the titration. The Kjeldahl nitrogen determination is conducted with a fully automatic Kjeltec™ 2400 auto sampler system. Some nitrogen-containing compounds, such as pyridine, alkaloids, and quinolone derivatives do not decompose easily during the digestion [105]. The measurement accuracy of the modified Kjeldahl method, when analyzing nitrogen in black liquor, is 95% ± 10% according to KCL Kymen Laboratoriot Oy [106]. A study conducted by KCL Kymen Laboratoriot Oy on the reliability of the modified Kjeldahl method with model cyclic nitrogen

compounds founded that between 67-103% of the cyclic nitrogen compounds were recovered [107].

3.1.2.2 Thermo Fisher Scientific FLASH 2000 organic element analyzer

Besides the modified Kjeldahl analysis method, the nitrogen content of selected samples was analyzed also with a Thermo Fisher Scientific FLASH 2000 organic element analyzer (FLASH 2000). In the FLASH 2000 analysis, the sample (2 ± 0.2 mg) was packed in a tin cup. The tin cup containing the sample was then oxidized at 950°C in pure oxygen. The exothermic reaction at elevated temperature between the sample and oxygen causes the temperature to rapidly increase up to 1800°C for a few seconds, thus converting the sample to gaseous products. The formed gases are led to a catalytic oxidation/reduction reactor. The gaseous nitrogen compounds are first oxidized fully with the help of copper oxide to NO_x and then reduced with electrolytic copper to N_2 . The formed gases are separated by gas chromatography and quantified with a thermal conductivity detector.

3.1.2.3 Cyanate analysis

The cyanate content in selected samples was analyzed by dissolving the samples in ultrapure water and filtering the solution through a $0.45\ \mu\text{m}$ filter. The cyanate in the filtrate was separated from other anions by ion chromatography using a Metrosep Anion Dual 2 column with a $2.0\ \text{mmol/L}$ sodium bicarbonate, $1.3\ \text{mmol/L}$ sodium carbonate eluent flowing at a $0.8\ \text{ml/min}$ rate [108]. In some experiments, a Metrosep A Supp 5 - $250/4.0$ column with a $1.0\ \text{mmol/L}$ sodium bicarbonate, $3.2\ \text{mmol/L}$ sodium carbonate eluent flowing at a $0.7\ \text{ml/min}$ rate was used for peak separation. The separated cyanate peak was quantified with a conductivity detector. Two similar ion chromatography systems were used during this work to determine cyanate. Both were manufactured by Metrohm AG, but the one was newer than the other. The injection of the sample was more reliable and the conductivity detector used to quantify the peaks was more accurate in the newer ion chromatography system compared to the older system.

This means that high standard deviations shown in some results originated from errors in the analysis itself. Figure 13 shows the cyanate analysis of four black liquor smelts prepared in an identical manner with the single particle reactor and dissolved separately in four different solutions and analyzed for cyanate with the newer ion chromatograph. The standard deviations shown in Figure 13 were calculated from six injections of each solution. This reliability study was conducted in order to determine the variations among identically-prepared samples. The error bars in the Results section of this thesis represent the standard deviation of six analyses conducted on one solution.

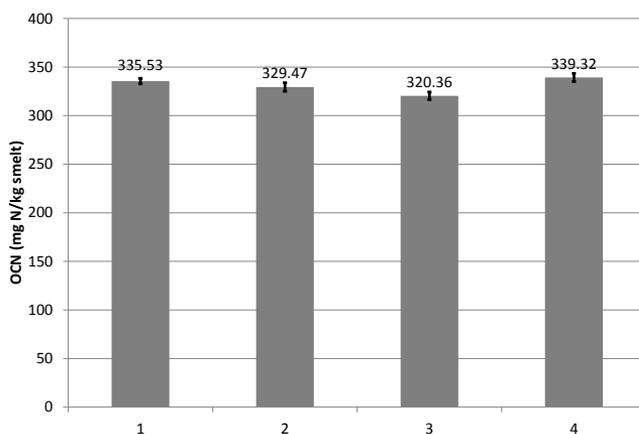


Figure 13. Cyanate analysis of four set of black liquor smelts dissolved and analyzed independently.

3.2 Materials

3.2.1 Modified black liquors

3.2.1.1 Black liquor - biosludge mixture

Three sampling campaigns: one in December 2010 and two sampling campaigns, May 19-20 and May 30-31, 2011, were conducted to obtain samples from a Finnish pulp mill before and after the addition of biosludge to black liquor evaporation. During the winter, biosludge was co-combusted with bark in

the power boiler at the mill. The power boiler was shut down during the summer and the biosludge was mixed with black liquor and co-combusted in the recovery boiler. The addition of biosludge to black liquor evaporation started on May 23, 2011. The pulp mill has three digesters: one for softwood, one for hardwood, and one for sawdust pulping. The spent cooking liquors from the digesters were mixed before going to a seven-effect evaporation set. The high-volume low-concentration gases (HVLC) formed during pulping and evaporation were burned in the recovery boiler, and the HVLC gases formed during green liquor causticization were burned in the lime kiln. Methanol and non-condensable gases (NCG) from the stripper were burned in a separate NCG boiler. Samples were collected from different stages of evaporation, as shown in Figure 14.

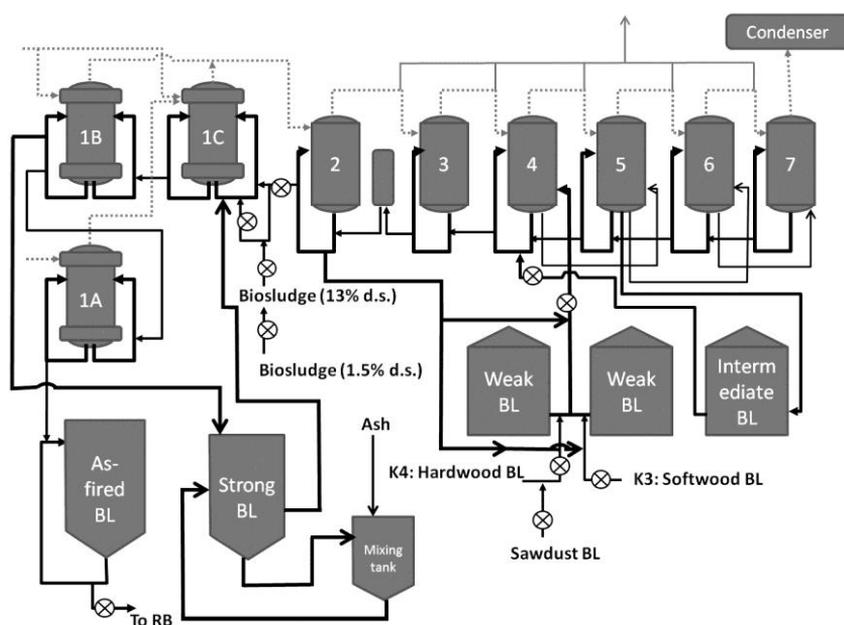


Figure 14. Sampling points in black liquor evaporation plant. Figure from **Paper I**.

Green liquor samples from the dissolving tank were also collected. Two samples, morning and afternoon, were collected each sampling day, resulting in

a total of eight samples per sampling location. Four samples were taken during biosludge addition and four prior to biosludge addition. During the period when biosludge was added, biosludge samples before and after mechanical dewatering were collected. The amount of biosludge added to the black liquor was roughly 0.5-1.2 wt% on a dry solids basis. Process data from the lime kiln, NCG boiler and recovery boiler were obtained from the mill to determine the impact of biosludge addition to a pulp mill's NO_x emissions. The fate of biosludge nitrogen was also studied at the laboratory scale by NO formation during combustion, and through cyanate formation experiments.

In the combustion experiments, six droplets (10 ± 0.5 mg) of each as-fired black liquor sample were burned at 1100°C 3.3% O₂ in N₂. The combustion characteristics of the as-fired black liquor samples are shown in Table II. The devolatilization and char burning time were determined from the digital video recorded during the combustion experiments, and the maximum swollen volume was determined from a captured image from the digital video. The data in Table II show a slight increase in the char burning time and the maximum swollen volume when biosludge was added. The combustion characteristics are discussed in detail in **Paper I**. The formed NO during the combustion experiments was analyzed. In the cyanate formation experiments, six droplets (14 ± 1 mg) of each as-fired black liquor sample were pyrolyzed at 800°C 100% N₂ for 10 seconds to form chars, and the chars were then gasified at 800°C 13% CO₂ in N₂ to smelt. The laboratory-made smelts and collected green liquor samples were analyzed for cyanate.

Table II. Combustion characteristics of the collected as-fired black liquors, combustion experiments conducted at 1100°C 3.3% O₂ in N₂ in the single particle reactor. Data from **Paper I**.

| | | Devolatilization Time (s) | | Char burning Time (s) | | Total combustion Time (s) | | Maximum swollen volume cm ³ /g d.s. | |
|----------------------------------|-----------|------------------------------|-------|--------------------------|-------|------------------------------|-------|---|-------|
| | | avg | stdev | avg | stdev | avg | stdev | avg | stdev |
| Without biosludge addition | 19 May AM | 1.6 | 0.2 | 6.4 | 0.4 | 8.0 | 0.4 | 50 | 13 |
| | 19 May PM | 1.6 | 0.2 | 6.1 | 0.4 | 7.7 | 0.3 | 73 | 27 |
| | 20 May AM | 1.9 | 0.1 | 5.6 | 0.5 | 7.6 | 0.5 | 69 | 19 |
| | 20 May PM | 2.0 | 0.2 | 5.5 | 0.8 | 7.4 | 0.6 | 60 | 16 |
| Average of all experiments | | 1.8 | 0.3 | 5.9 | 0.6 | 7.7 | 0.5 | 62 | 19 |
| With biosludge addition | 30 May AM | 1.8 | 0.2 | 7.3 | 0.4 | 9.1 | 0.4 | 81 | 37 |
| | 30 May PM | 1.7 | 0.3 | 7.8 | 0.5 | 9.5 | 0.4 | 64 | 27 |
| | 31 May AM | 1.4 | 0.1 | 7.2 | 0.7 | 8.7 | 0.7 | 77 | 17 |
| | 31 May PM | 1.6 | 0.1 | 6.6 | 0.6 | 8.3 | 0.5 | 76 | 25 |
| Average of all experiments | | 1.6 | 0.2 | 7.3 | 0.7 | 8.9 | 0.7 | 75 | 26 |

3.2.1.2 Reduced lignin black liquors

The removal of lignin from Kraft black liquor samples (softwood and eucalyptus) was performed by Innventia in a pilot scale facility. Four samples were obtained from Innventia: softwood and eucalyptus black liquor samples, and filtrate samples from those black liquors from which lignin had been partially removed. The original black liquor and the filtrate sample were mixed to obtain two intermediate levels of lignin removal for both softwood and eucalyptus liquors. The received and mixed samples had an initial dry solids content of less than 25%; they were then dried in an oven at 105°C to 85% dry solids.

The soda samples used in this work were obtained from Valmet Power Oy. The soda liquor was generated in a laboratory scale digester, and the lignin removal from the soda liquor was performed by Chalmers Technical University in Gothenburg. One soda liquor and two samples with different levels of lignin removal were obtained. The soda samples had an initial dry solids content of less than 41%, and were dried at 105°C to 75% dry solids content. The lignin content of the samples used is shown in Table III.

Table III. The lignin content of the reduced lignin liquor samples (*calculated based on the black liquor and filtrate analysis). Data from **Paper II**.

| | | Lignin content mg / g d.s. |
|------------|-------------------|-------------------------------|
| Softwood | Black Liquor | 366 |
| Softwood | 10% Lower Lignin | 329* |
| Softwood | 25% Lower Lignin | 275* |
| Softwood | Filtrate | 166 |
| Eucalyptus | Black Liquor | 429 |
| Eucalyptus | 10% Lower Lignin | 386* |
| Eucalyptus | 25% Lower Lignin | 313* |
| Eucalyptus | Filtrate | 242 |
| Soda | Black Liquor | 391 |
| Soda | 8.4% Lower Lignin | 358 |
| Soda | 30% Lower Lignin | 274 |

The combustion experiments for the reduced lignin liquors were conducted in the single particle reactor by burning six droplets (10 ± 0.5 mg) of each sample at 900°C 10% O_2 in N_2 , after which the formed NO was measured. The combustion characteristics of the reduced lignin liquors are shown in Table IV. The devolatilization time, char burning time, and the maximum swollen volume were determined in the same manner as for the black liquor – biosludge mixtures. The data in Table IV show that the maximum swollen volume was lowest for all of the filtrate samples. For softwood samples, the combustion times decreased and the swelling increased with increasing lignin removal, except the filtrate sample. The opposite was observed for the eucalyptus and the soda samples. The combustion characteristics of the reduced lignin liquors are discussed in detail in **Paper II**. The cyanate formation experiments were conducted by pyrolyzing six droplets (10 ± 0.5 mg) of each sample at 800°C 100% N_2 for 10 seconds to form chars, and the chars were then gasified at 800°C 13% CO_2 in N_2 to form a smelt. The formed smelts were analyzed for cyanate with ion chromatography.

Table IV. Combustion characteristics of reduced lignin liquors, combustion experiments conducted at 900°C 10% O₂ in N₂ in the single particle reactor. Data from **Paper II**.

| | | Devolatilization | | Char burning | | Total combustion | | Maximum swollen volume | |
|------------|-------------------|------------------|-------|--------------|-------|------------------|-------|-------------------------|-------|
| | | Time (s) | | Time (s) | | Time (s) | | cm ³ /g d.s. | |
| | | avg | stdev | avg | stdev | avg | stdev | avg | stdev |
| Softwood | Black Liquor | 1.3 | 0.2 | 6.0 | 0.6 | 7.4 | 0.7 | 49 | 9 |
| Softwood | 10% Lower Lignin | 1.3 | 0.2 | 6.0 | 0.4 | 7.2 | 0.3 | 60 | 15 |
| Softwood | 25% Lower Lignin | 1.1 | 0.1 | 5.2 | 0.4 | 6.3 | 0.5 | 66 | 37 |
| Softwood | Filtrate | 0.8 | 0.1 | 4.6 | 0.5 | 5.4 | 0.6 | 19 | 2 |
| Eucalyptus | Black Liquor | 1.6 | 0.2 | 4.3 | 1.1 | 6.0 | 1.1 | 97 | 39 |
| Eucalyptus | 10% Lower Lignin | 1.1 | 0.2 | 5.9 | 0.9 | 7.0 | 0.8 | 58 | 9 |
| Eucalyptus | 25% Lower Lignin | 1.4 | 0.3 | 6.3 | 0.8 | 7.7 | 0.8 | 32 | 8 |
| Eucalyptus | Filtrate | 1.1 | 0.3 | 5.5 | 0.9 | 6.6 | 0.8 | 17 | 2 |
| Soda | Black Liquor | 1.5 | 0.1 | 4.8 | 0.5 | 6.3 | 0.5 | 115 | 44 |
| Soda | 8.4% Lower Lignin | 1.6 | 0.3 | 6.0 | 0.9 | 7.6 | 1.0 | 72 | 17 |
| Soda | 30% Lower Lignin | 2.1 | 0.4 | 7.8 | 0.5 | 9.9 | 0.8 | 11 | 3 |

3.2.1.3 Black liquor mixed with solid biomass

Black liquor with initial dry solids of 80.4% was mixed with dried wood, bark, and peat. Peat was only used in the cyanate formation experiments to clarify the fate of the nitrogen in the added fuel. Peat is not considered a CO₂ neutral fuel and is not expected to be incinerated with black liquor in the recovery boiler. The dry solids content and the physical size of the solid biomass samples are given in Table V. For the combustion experiments, biomass was mixed with black liquor in ratios varying from 13-50% on a dry solids basis. For the cyanate experiments only one level of addition was used.

Table V. Size and dry solids of the samples used. Data from **Paper III**.

| | dry solids (wt-%) | size |
|--------------|----------------------|---|
| Black Liquor | 80.36 | liquid |
| Wood | 92.23 | length (up to 4 mm) width (up to 2 mm) |
| Bark | 92.28 | < 1 mm |
| Peat | 96.65 | ground |

The combustion experiments of the mixtures were conducted by burning six droplets (14 ± 1 mg) of each sample at 900°C 10% O_2 in N_2 and the formed NO was measured. The combustion characteristics of the black liquor biomass mixtures can be seen in Table VI. The devolatilization time, char burning time, and the maximum swollen volume were determined in the same manner as for the black liquor – biosludge mixtures. The data in Table VI show that the char burning time increased with increasing biomass addition, and that the swelling decreased compared to pure black liquor. The combustion characteristics of the black liquor biomass mixtures are discussed in detail in **Paper III**. In the cyanate formation experiments, six droplets (12 ± 1 mg) were pyrolyzed at 800°C 100% N_2 for 6 seconds to form chars, and the chars were then gasified at 800°C 13% CO_2 in N_2 to different levels of char conversion. The char conversion yield was determined by comparing the weight of the formed char to the weight of a sample in which all of the organic material was volatilized and only smelt remained. The residues and smelts after gasification were analyzed for cyanate with ion chromatography.

Table VI. Combustion properties of the collected black liquor biomass mixtures, combustion experiments conducted at 900°C 10% O_2 in N_2 in the single particle reactor. Data from **Paper III**.

| | Devolatilization | | Char burning | | Total combustion | | Maximum swollen volume | |
|---------------------------|------------------|-------|--------------|-------|------------------|-------|-----------------------------|-------|
| | Time (s) | | Time (s) | | Time (s) | | $\text{cm}^3/\text{g d.s.}$ | |
| | avg | stdev | avg | stdev | avg | stdev | avg | stdev |
| BL | 1.4 | 0.3 | 6.2 | 0.6 | 7.8 | 0.7 | 59 | 12 |
| 86.8% BL + 13.2% dry bark | 3.2 | 0.4 | 10.3 | 2.5 | 13.6 | 2.6 | 39 | 16 |
| 74.4% BL + 25.6% dry bark | 3.1 | 0.6 | 10.4 | 5.3 | 13.7 | 5.6 | 32 | 9 |
| 65% BL + 35% dry bark | 3.6 | 0.4 | 13.8 | 2.9 | 17.4 | 3.1 | 20 | 5 |
| 50% BL + 50% dry bark | 3.1 | 0.2 | 19.4 | 4.2 | 22.5 | 4.4 | 18 | 6 |
| dry bark | 3.1 | 0.8 | 45.1 | 4.5 | 48.0 | 5.2 | - | - |
| BL | 1.4 | 0.3 | 6.2 | 0.6 | 7.8 | 0.7 | 59 | 12 |
| 86.8% BL + 13.2% dry wood | 2.4 | 0.4 | 9.2 | 1.9 | 11.5 | 1.9 | 34 | 11 |
| 74.4% BL + 25.6% dry wood | 3.1 | 0.3 | 14.1 | 4.2 | 17.2 | 4.4 | 23 | 7 |
| 65% BL + 35% dry wood | 3.2 | 0.3 | 13.5 | 2.2 | 16.7 | 2.2 | 20 | 9 |
| 50% BL + 50% dry wood | 3.0 | 0.3 | 13.9 | 2.4 | 17.0 | 2.5 | 24 | 4 |
| dry wood | 5.7 | 0.5 | 24.8 | 0.8 | 30.5 | 1.2 | - | - |

3.2.2 Materials used in gasification of alkali metal loaded fuels

Fuel samples of different geological age and nitrogen content (bark, peat, and coal) were used in studying the formation of cyanate during gasification of alkali metal loaded fuels. The ash contents and concentrations of selected inorganic compounds are shown in Table VII. The inorganic content of the samples was analyzed by different laboratories for different projects, which explains why, for example, the limits of quantification for chloride in bark and peat were different. The fuels were loaded with different alkali and alkali earth metal salts (KCl, K_2CO_3 , K_2SO_4 , Na_2CO_3 , and $CaCO_3$), and the initial amount of the cation in the fuel was taken into account when calculating the amount of salt needed. The levels of salt loading (on a cation basis) were 1, 5, 10, and 15 wt%. The procedure for loading the alkali metals was the following: the amount of sample was weighed, and the amount of salt needed to obtain the desired level of cation loading in the weighed sample was calculated. The amount of salt was weighed, dissolved in ultrapure water, and mixed with the weighed sample. The mixture was stirred overnight and then dried at 105°C for 24 hours. The dried mixture was ground to a powder prior to the experiments. Due to the low solubility of $CaCO_3$, it was only partially dissolved before mixing it with the sample.

Table VII. Ash content and concentration of selected inorganic compounds (samples ashed at 550°C for 300 minutes). Data from **Paper IV**.

| | Ash (wt-%) | K | Na | Ca | S | Cl | Si |
|------|---------------|------------------|-----|------|------|------|-------|
| | | (mg/kg dry fuel) | | | | | |
| Bark | 2.65 | 1700 | 200 | 4700 | 490 | 140 | 1800 |
| Coal | 13.75 | 1310 | 637 | 7470 | 4630 | 0 | 32900 |
| Peat | 3.34 | 270 | 171 | 4320 | 1890 | <500 | 4490 |

To study the cyanate formation during gasification, the samples (15±0.5 mg) were placed on quartz glass holders and pyrolyzed for 10 seconds at 800°C in 100% N₂ to form chars. The chars were then gasified in 13% CO₂ / 87% N₂ at 800-1000°C for different times to obtain different levels of char conversion. The nitrogen content of the fuel samples and pyrolyzed catalyst loaded fuel samples

were analyzed with the modified Kjeldahl method or with the Thermo Fisher Scientific FLASH 2000 organic element analyzer. After gasification, the cyanate content of the residues was analyzed by ion chromatography.

3.2.3 Samples in the formation and decomposition of black liquor cyanate

In the cyanate formation and decomposition experiments, one hardwood and one softwood Kraft black liquor were used. The liquors had an initial dry solids content of roughly 20% and were dried to 75% dry solids. Cyanate formation during pyrolysis was determined by pyrolyzing 10 ± 0.5 mg droplets in the single particle reactor in 100% N_2 at 800-1000°C for different times. Cyanate formation during char gasification was determined by first pyrolyzing 10 ± 0.5 mg droplets in the single particle reactor in 100% N_2 at 800°C for 30 seconds to form a char. The formed chars were then gasified in CO_2 concentrations ranging from 13-50% in N_2 at 800-1000°C for different times to obtain different levels of char conversion. In the smelt cyanate decomposition experiments, 10 ± 0.5 mg hardwood black liquor droplets were first gasified at 800°C 13% CO_2 in N_2 and at 900°C 13% CO_2 in N_2 for different times to obtain a smelt, and to determine the stability of cyanate in CO_2 -containing atmospheres. After a smelt was obtained, the sample was kept inside the reactor while the gas composition was quickly changed from 13% CO_2 in N_2 to 100% N_2 , 3% O_2 in N_2 , or 13% CO_2 + 3% O_2 in N_2 . The formed smelts were exposed from 30 seconds to 7 minutes inside the reactor in order to determine the cyanate decomposition. The decomposition of smelt cyanate in CO_2 containing atmosphere at 900°C was also tested by prolonged gasification experiments. The residues and smelts after each experiment were analyzed by ion chromatography for cyanate. The NO formation was measured during the longest char gasification and cyanate decomposition experiments.

4 RESULTS AND DISCUSSION

4.1 Fate of biosludge nitrogen in black liquor evaporation and combustion

The objective of this study was to determine the fate of the added biosludge nitrogen in the chemical recovery cycle, as questions remained after a previous mill sampling campaign [35]. The nitrogen content, as mg N/kg black liquor dry solids (analyzed with modified Kjeldahl method), of the black liquor from different stages of evaporation is shown in Figure 15. The dashed gray line shows the nitrogen content of samples collected in December 2010 when no biosludge was added, and the solid and dotted black lines indicate when biosludge was added to the black liquor after the second effect. Roughly 20% of the nitrogen in the black liquor was removed during the early stages of evaporation, which was consistent with previous studies [35, 67, 78]. The nitrogen content remained constant during the rest of the evaporation when no biosludge was added. The added biosludge had an average 5.3 wt% (dry basis) nitrogen content of which 0.3 wt% was NH_3 ; the addition of biosludge increased the nitrogen content of the black liquor, as shown in Figure 15. The cause of the nitrogen content increase prior to biosludge addition in the samples collected on the afternoon of May 31 (data point indicated with a circle) remains unknown. The increase may be attributable to the fluctuation in the black liquor nitrogen content. Only one sample per data point per sampling run was collected, and the variation in black liquor nitrogen content during a 6-hour sampling run was not determined.

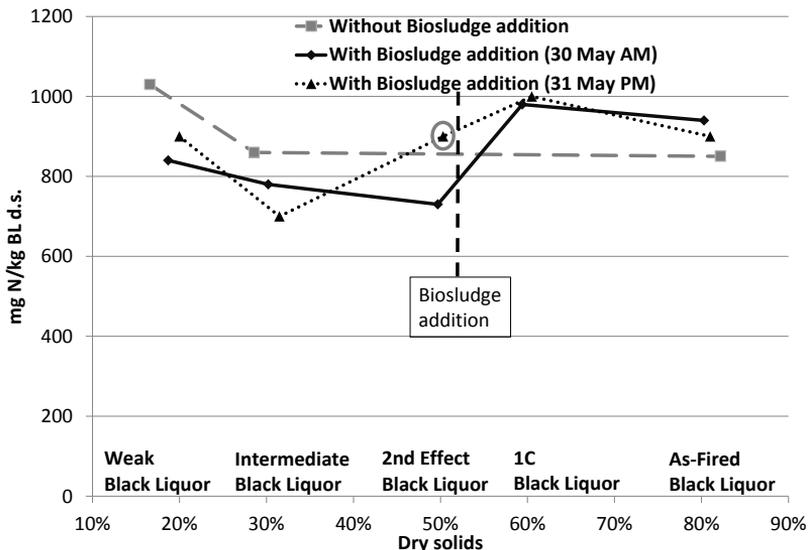


Figure 15. Nitrogen content of black liquor during different stages of evaporation. Figure from **Paper I**.

The nitrogen concentrations of the collected as-fired black liquor samples are shown in Table VIII. The addition of biosludge increased the nitrogen content of the as-fired black liquor by approximately 30%. Recovery boilers’ NO_x emissions (g N/kg black liquor dry solids), black liquor firing (kg/s dry solids), and the amount of biosludge added (kg/s dry solids) during a 15-day period are shown in Figure 16. The addition of biosludge started on May 23, but no clear increase in the recovery boilers’ NO_x was detected. The only increases in NO_x occurred when the black liquor firing rate suddenly dropped.

Table VIII. Nitrogen content of the as-fired black liquors. Table from **Paper I**.

| Black Liquor Sample | | | Kjeldahl-N (wt-% d.s.) As-Fired Black Liquor |
|---------------------|--------|----|---|
| Before | 19 May | AM | 0.069 |
| Biosludge Addition | | PM | 0.069 |
| After | 20 May | AM | 0.066 |
| Biosludge Addition | | PM | 0.068 |
| After | 30 May | AM | 0.094 |
| Biosludge Addition | | PM | 0.088 |
| After | 31 May | AM | 0.090 |
| Biosludge Addition | | PM | 0.092 |

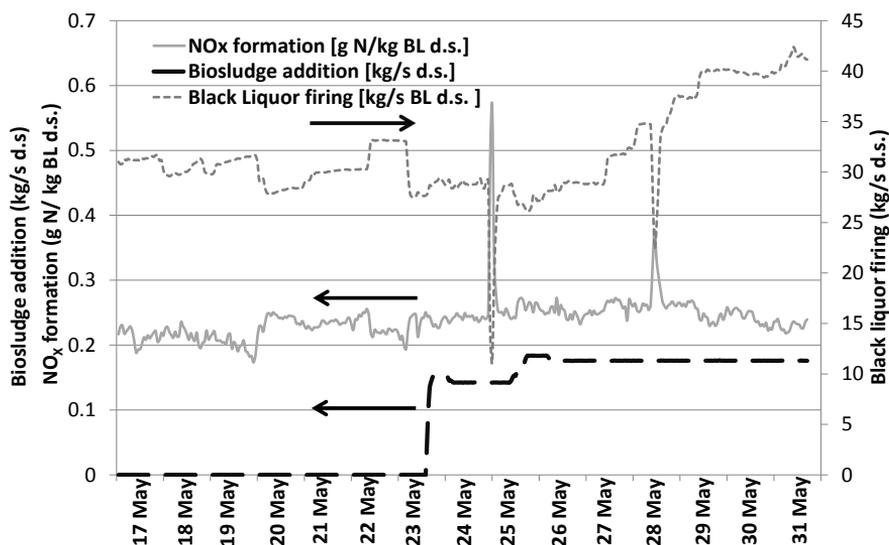


Figure 16. NO_x formation, black liquor firing rate, and biosludge addition during a 15-day period. Figure from **Paper I**.

The NO formation (g N/kg black liquor dry solids) during combustion experiments in the single particle reactor at 1100°C 3.3% O₂ / 96.7% N₂ for the as-fired black liquor samples (Table VIII) is shown in Figure 17. The dotted vertical line represents the average NO formed of the four as-fired black liquor samples before and after biosludge addition. The NO formation was on average 30% higher from the samples with added biosludge during the droplet combustion experiments in the single particle furnace. Comparing the amount of NO formed in Figure 17 and the nitrogen content of the as-fired black liquors, Table VIII, the conversion of black liquor nitrogen to NO was between 67-75%. In laboratory experiments, the smelt nitrogen is also oxidized and at least partially forms NO. In recovery boilers, due to reducing conditions in the lower furnace, the smelt nitrogen exits the recovery boiler and the conversion of black liquor nitrogen to NO is much lower. Combustion is an exothermic reaction and due to the high temperature used in the combustion experiments, it is entirely possible that the temperature on the surface of the droplets rises momentarily

above 1400°C. This spike in temperature can cause a portion of the formed NO to originate from thermal NO_x.

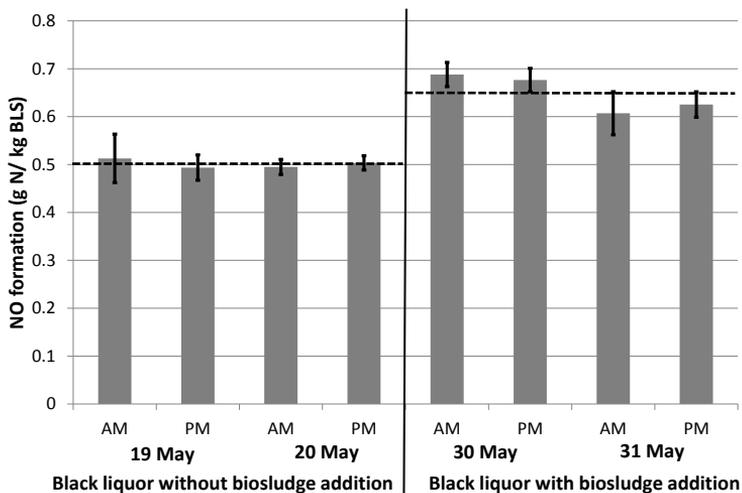


Figure 17. NO formation of as-fired black liquors at 1100°C 3.3% O₂ in N₂. Error bars represent the standard deviations of six separate droplets burned in the single particle reactor. Figure from **Paper I**.

The cyanate content of collected mill green liquors is shown in Figure 18, and the as-fired black liquor smelts are shown in Figure 19. The dotted lines in these figures represent the average cyanate content of the four samples. The as-fired black liquor samples were pyrolyzed (800°C 100% N₂) for 10 seconds to form chars, and the chars were then gasified (800°C 13% CO₂/87% N₂) to smelt. In both mill green liquors and the smelts, the amount of cyanate increased by roughly 40% with biosludge addition, which corresponds to roughly 60% of the biosludge nitrogen. The remaining 40% of the biosludge nitrogen was most likely released during pyrolysis. This pyrolysis nitrogen does not lead to any noticeable increase in the recovery boiler NO. The increased cyanate is assumed to result in higher overall nitrogen emissions as cyanate reacts with water to form NH₃. The NH₃ is found in the vent gases, in methanol, and in non-condensable gases (NCG) from the stripper, all of which are ultimately burned, but in different devices.

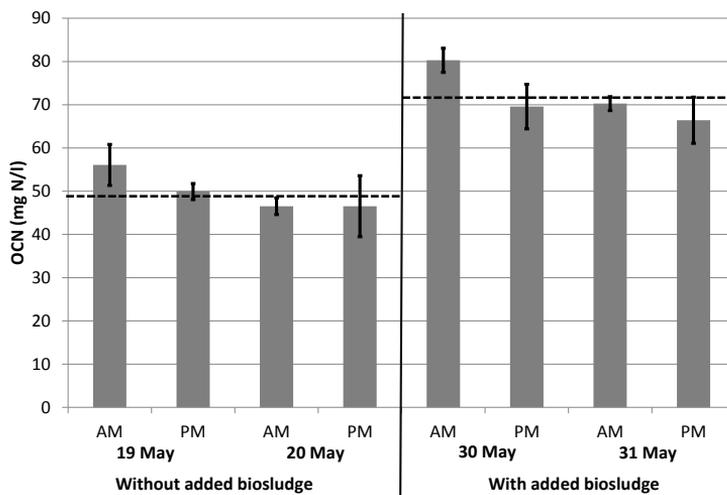


Figure 18. Cyanate content of the mill green liquors. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper I**.

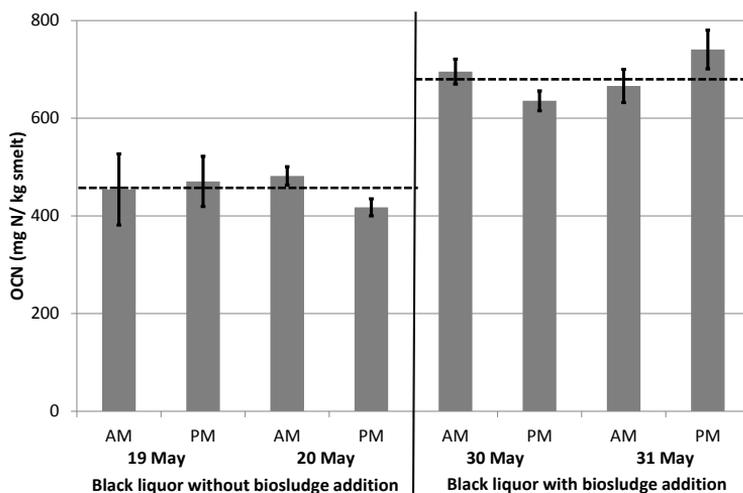


Figure 19. Cyanate in laboratory made smelts of the as-fired black liquor samples. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper I**.

The addition of biosludge, as well as the NO_x concentrations (mg N/Nm³) in the NCG boiler and the lime kiln flue gas, is shown in Figure 20. No clear increase in the NO_x concentration in the lime kiln flue gas was detected after the biosludge addition started. The lime kiln used natural gas as fuel and burned the high-volume low-concentration NCGs from recausticizing. The methanol and high-concentration NCG from the stripper were burned in the NCG boiler. The 19-day average of NO_x formed prior to biosludge addition was 336 mg N/Nm³ and the 22-day average after biosludge addition was 407 mg N/Nm³. The addition of biosludge increased the NO_x formation from the NCG boiler by 21%. This would indicate that the added biosludge nitrogen results in increased NH₃ formation. Part of the NH₃ exited recausticizing with the white liquor and was collected in the dirty condensates from the pulp mill digesters and evaporators. The dirty condensates were stripped and the NH₃ ended up partly in the methanol and partly in the NCG from the stripper, both of which were burned in the NCG boiler.

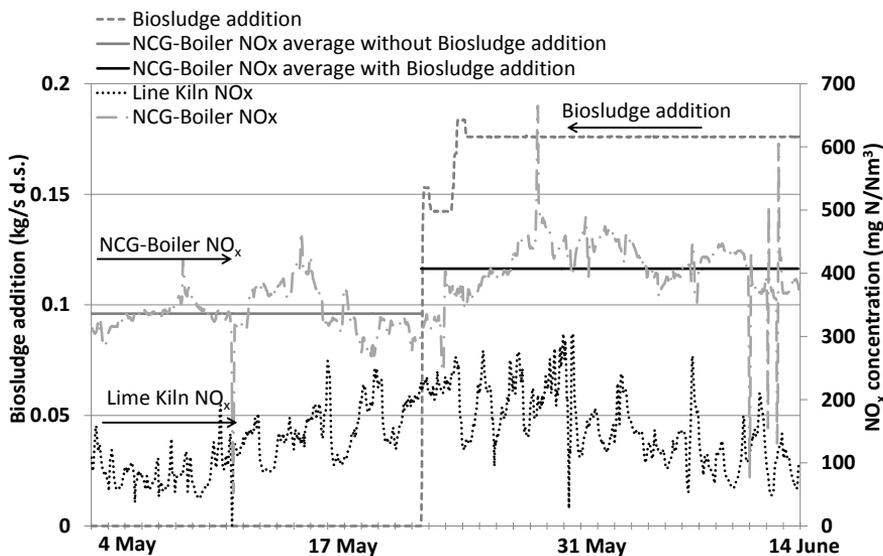


Figure 20. NO_x concentration in lime kiln and NCG boiler flue gas. Figure from Paper I.

The results from this work showed that volatile nitrogen compounds are released from black liquor in the early stages of evaporation, and the addition of biosludge to the intermediate liquor increased the nitrogen content of black liquor. Both observations were consistent with previous studies [35, 70, 78]. The increased nitrogen content of the black liquor did not affect the NO formation in the recovery boiler, while laboratory combustion experiments showed an increase in NO formation. Both green liquor samples from the mill and laboratory made smelt samples showed that the addition of biosludge increased the amount of formed cyanate. In the previous study by Kymäläinen et al. [35] the concentrator gases, stripper gases and methanol were fed in to the recovery boiler thus the fate of biosludge nitrogen was not clearly identified. In this work the methanol and high-concentration NCG from the stripper were burned in the NCG boiler, where an increase in NO formation was detected after biosludge addition. This study clarified the fate of biosludge nitrogen in the chemical recovery cycle.

4.2 NO formation in modified black liquors combustion

4.2.1 NO formation in reduced lignin black liquor combustion

The nitrogen content of the reduced lignin black liquor samples is shown in Table IX. From Table IX it can be seen that lignin removal decreased the nitrogen content of the black liquor.

Table IX. Nitrogen content of the reduced lignin black liquors. Data from **Paper II.**

| | Softwood Kjeldahl N (wt-% d.s.) | Eucalyptus Kjeldahl N (wt-% d.s.) |
|------------------|---------------------------------------|---|
| Black Liquor | 0.062 | 0.086 |
| 10% Lower Lignin | 0.060* | 0.082* |
| 25% Lower Lignin | 0.057* | 0.077* |
| Filtrate | 0.052 | 0.070 |

*calculated based on the analysis of Black Liquor and Filtrate

| | Soda Kjeldahl N (wt-% d.s.) |
|-------------------|-----------------------------------|
| Black Liquor | 0.071 |
| 8.4% Lower Lignin | 0.066 |
| 30% Lower Lignin | 0.063 |

The NO formation (as g N/kg black liquor dry solids) during laboratory-scale combustion experiments for the reduced lignin Kraft liquors are shown in Figure 21 and for the soda samples in Figure 22. The NO formation shown in Figure 21 and Figure 22 includes the NO formed during pyrolysis, char burning and smelt oxidation. The NO formation decreased with increasing lignin removal for the Kraft liquor samples. The decrease was due to the lower nitrogen content in reduced lignin samples, Table IX. The share of black liquor nitrogen to NO conversion was roughly 40% for the eucalyptus samples and 45% for the softwood samples. For the soda samples, the amount of NO formed was roughly equal for all of the samples. The nitrogen content in the soda samples also decreased with increasing lignin removal. The maximum swollen volume of the soda samples decreased dramatically with increasing lignin removal, which means a decrease in char surface area. This could have an impact on NO formation because biomass combustion experiments had been shown that the released NO from inside the particle was reduced by the char to N₂ [109, 110]. One possible explanation for the increase in NO formation is that the decrease in

maximum swollen volume leads to less char surface where the released NO can be reduced back to N_2 . More work is required to clarify the reason behind the increase in NO formation from reduced soda liquors. The black liquor nitrogen to NO conversion was 45% for the original soda sample and increased to roughly 55% for the 30% lower lignin sample. The liquor samples should burn slightly hotter than the filtrate samples as the HHV of black liquor is higher than the HHV of the filtrates [102]. The combustion experiments were conducted at 900°C and it was assumed that the temperature in the combustion zone was below temperature needed for of thermal NO_x , thus the NO measured originated only from the black liquor nitrogen [71]. The slightly higher combustion temperature may have affected NO formation and reduction reactions from this fuel nitrogen. However, the amount of fuel nitrogen is expected to be the more important variable.

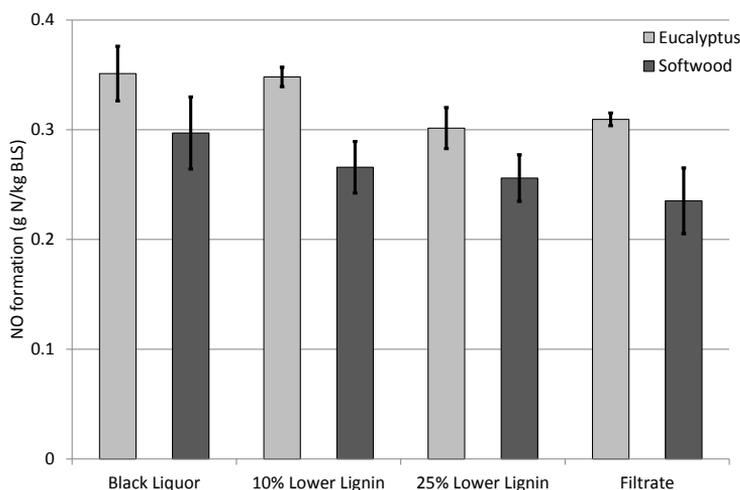


Figure 21. NO formation of softwood and eucalyptus samples. Combustion experiments conducted at 900°C 10% O_2 in N_2 . Error bars represent the standard deviations of six separate droplets burned in the single particle reactor. Figure from **Paper II**.

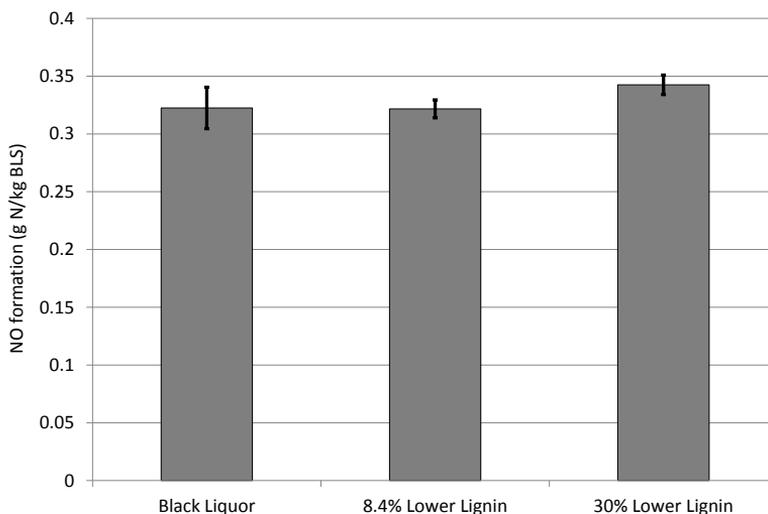


Figure 22. NO formation of soda samples. Combustion experiments conducted at 900°C 10% O₂ in N₂. Error bars represent the standard deviations of six separate droplets burned in the single particle reactor. Figure from **Paper II**.

4.2.2 NO formation in combustion of black liquor solid biomass mixtures

The nitrogen content of the black liquor and biomasses used to make the black liquor – biomass mixtures are shown in Table X. The biomass used in this work had a higher nitrogen content than black liquor, which resulted in fuel mixtures with a higher nitrogen content than the black liquor.

Table X. Nitrogen content of black liquor and biomass fuels. Data from **Paper III**.

| Fuel | Kjeldahl N (wt-% d.s.) |
|--------------|---------------------------|
| Black Liquor | 0.08 |
| Wood | 0.2 |
| Bark | 0.4 |
| Peat | 2.06 |

The amount of NO formed (g N/kg dry fuel) during combustion (900°C 10% O₂ in N₂) for the black liquor and biomass (dry bark and dry wood) mixtures are shown in Figure 23. The x-axis label in Figure 23 describes the share of black liquor and biomass in the fuel mixtures. Wood and bark each have higher nitrogen contents than black liquor, Table X, and the mixtures have 1.2 to 2 times more nitrogen than the nitrogen content of the black liquor. The amount of NO formed was higher for black liquor-biomass mixtures than for pure black liquor. More NO was formed from the black liquor-bark mixtures than from black liquor-wood mixtures because bark had higher nitrogen content than wood. Roughly two times more NO was formed from the dried bark than from the dried wood.

The amount of formed NO from the black liquor mixed with different levels of biomass was quite similar. There are several possible explanations for this. The used bark was in < 1 mm uniform pieces, while the wood was in considerably larger pieces. These solid biomasses and liquid black liquor were mixed to obtain mixtures with different black liquor to biomass ratio. Due to this heterogeneous mixture and especially to the large particle size for the dried wood, the individual droplets made from a mixture did not necessarily have the same black liquor to biomass ratio as the mixture had. This variation in droplet composition also explains the standard deviations seen in Figure 23.

From the recorded video it was observed, that the added biomass particle remained at least partly inside the swollen black liquor char particle. It is assumed that the NO released from the biomass char is reduced inside the black liquor char, thus decreasing the amount of formed NO [109, 110]. The addition of biomass to black liquor also affected the maximum swollen volume of the black liquor droplet, which could have an impact on the NO formation.

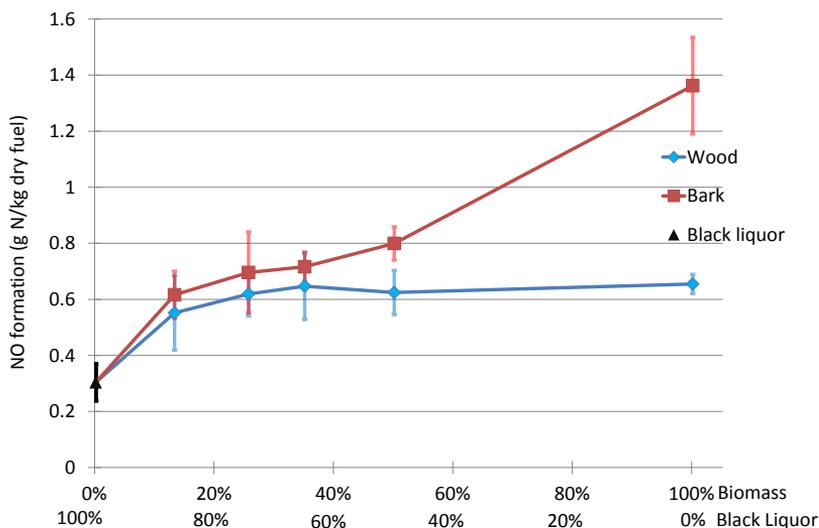


Figure 23. NO formation during combustion (900°C 10% O₂ in N₂) of black liquor, black liquor-biomass (dry bark and wood) mixtures, dry bark and dry wood. Error bars represent the standard deviation of six separate samples burned in the single particle reactor. Data from **Paper III**.

4.3 Cyanate formation and decomposition

This section of the thesis will focus on cyanate formation in modified black liquors other than from the addition of biosludge, which was covered in Section 4.1; cyanate formation during gasification of alkali metal loaded fuels; cyanate formation during thermal conversion of black liquor; and the decomposition of smelt cyanate.

4.3.1 Cyanate formation in modified black liquors

4.3.1.1 Cyanate formation in reduced lignin black liquors

Smelts from reduced lignin black liquor samples were produced by pyrolyzing (800°C 100% N₂) the samples for 10 seconds to chars. The formed chars were gasified (800°C 13% CO₂ in N₂) to smelt. The amount of cyanate in the smelts for the reduced lignin Kraft liquor samples is shown in Figure 24 and for the

soda samples in Figure 25. For all samples, at the lowest level of lignin removal (10% and 8.4% lower lignin), the amount of cyanate formed was equal to or slightly higher than the original liquor sample. The reason the cyanate content in the 10% lower lignin eucalyptus increased slightly could be attributable to the ratio between inorganic and organic compounds in the char, or simply to a higher char nitrogen content. Further work is needed to clarify this question. For the 25% lower lignin and filtrate Kraft liquor samples, the amount of cyanate in smelt were lower than for the original sample. The black liquor nitrogen to cyanate conversion for the softwood samples was between 47% and 62%, and for the eucalyptus samples between 40% and 50%.

Almost no cyanate was formed from the 30% lower lignin soda sample. One reason for this was that in these gasifying conditions, for some reason the sample did not form a smelt. The remaining residue still looked partially swollen and thus the char was not fully converted to smelt. It was speculated that nitrogen was still left in the organic char matrix, thus it was not released as volatile nitrogen compounds and did not form cyanate. The black liquor nitrogen to cyanate conversion for soda samples was between 2% and 14%, which was much lower than for the Kraft liquor samples. The lower amounts of cyanate formed from soda liquors could be due to the lack of sulfur in the soda liquors. Kraft liquor smelt consists mainly of a mixture of sodium carbonate and sodium sulfide, while soda liquor smelt consists mainly of sodium carbonate. The sodium carbonate - sodium sulfide mixture has a lower melting point than sodium carbonate. The Kraft black liquor smelt was in molten form while the soda liquor smelt did not melt, and there was some unreacted carbon in the smelt as indicated by the somewhat grey color with black specs. Whether it was that the smelt was not molten; that there was some unreacted char or some other reason is not clear. The reason behind the low amount of cyanate found in soda liquor smelt should be studied more.

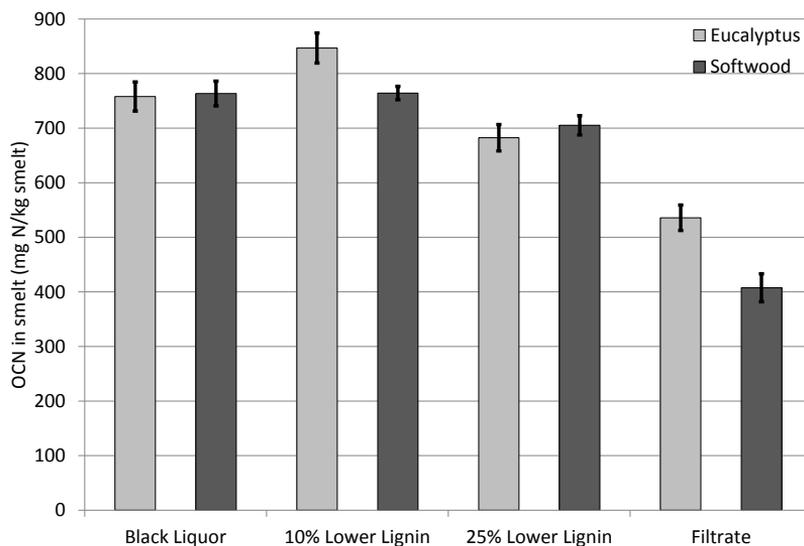


Figure 24. Amount of cyanate in smelts from softwood and eucalyptus Kraft liquor samples. Smelts were produced by pyrolyzing (800°C 100% N₂) the samples for 10 seconds to chars and gasifying (800°C 13% CO₂ in N₂) the chars to smelts. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper II**.

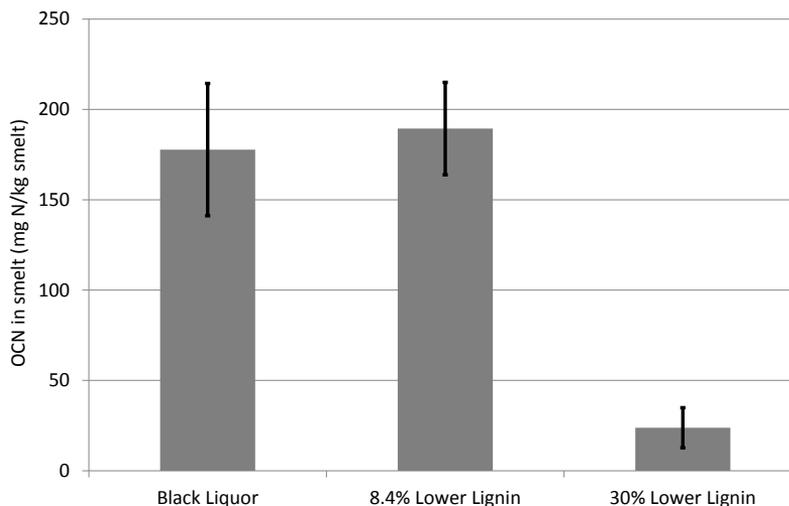


Figure 25. Amount of cyanate in smelts from soda samples. Smelts were produced by pyrolyzing (800°C 100% N₂) the samples for 10 seconds to chars and gasifying (800°C 13% CO₂ in N₂) the chars to smelts. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper II**.

4.3.1.2 Cyanate formation in black liquor – biomass mixtures

The cyanate formation during gasification of black liquor and black liquor-biomass mixtures to different levels of char conversion are shown in Figure 26. The cyanate formation was relatively slow in the beginning of the char gasification (< 50% of the char was converted), and the formation rate increased towards the end of char conversion. I speculate the reason for the increase in cyanate formation towards the end of the char conversion is that carbon is a stronger reducing agent than nitrogen, and thus carbonate and other oxygen containing species react primarily with char carbon until the carbon is almost depleted and then reacts with nitrogen.

The amount of cyanate formed was higher for the black liquor-fuel mixtures than for pure black liquor. The amount of cyanate formed from the black liquor-peat mixtures was more than the total nitrogen content of pure black liquor. This

clearly indicated not only that black liquor nitrogen is converted to cyanate, but also that black liquor acted as a catalyst and converted a portion of the nitrogen in peat to cyanate. The gasification of experiments with pure peat showed that peat nitrogen itself did not form cyanate. The fraction of fuel nitrogen converted to cyanate was clearly higher for black liquor than for black liquor-biomass mixtures, indicating that cyanate formation mechanisms are promoted more strongly in black liquor. This is probably due to the uniform distribution of alkali metals in the organic matrix of black liquor. The catalytic behavior of black liquor inspired the work of doping different fuels with different alkali metal salts.

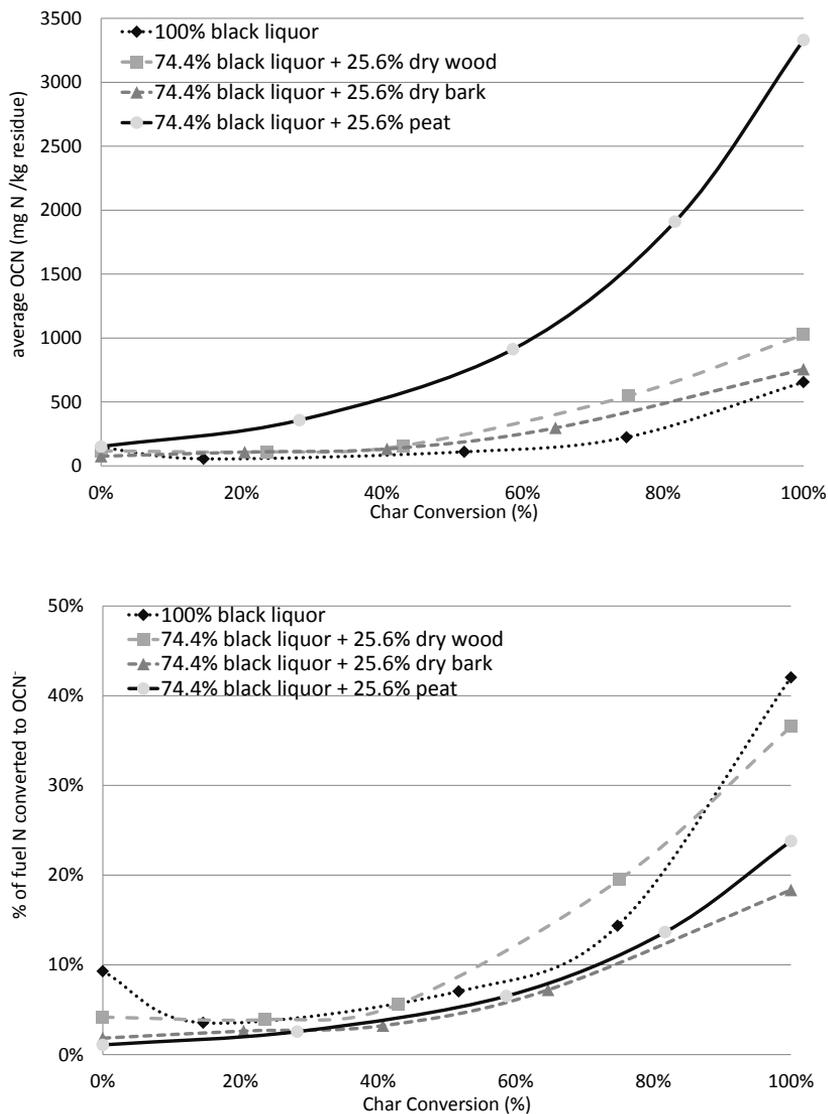


Figure 26. Cyanate formation during char conversion of black liquor and black liquor biomass mixtures. Amount of cyanate found in the residue (mg N/kg residue (top) and as a fraction of fuel nitrogen (bottom). The samples were pyrolyzed (800°C 100% N₂) for 6 seconds to form chars. The formed chars were gasified at 800°C 13% CO₂ in N₂ to different char conversion levels. Figures from **Paper III**.

4.3.2 Cyanate formation during gasification of alkali loaded fuels

This research was conducted purely to identify the reasons cyanate is formed during thermal conversion of black liquor. During this research, different fuels and alkali metal salts were used in order to shed light on the different parameters affecting cyanate formation.

The nitrogen content of fuel samples used in the cyanate formation experiments prior to alkali metal loading are shown in Table XI. These samples were analyzed by both methods: the modified Kjeldahl method and the Thermo Scientific FLASH 2000 Organic Element Analyzer. The two analysis methods yielded similar results, and on the basis of the results, further nitrogen analysis in this study was conducted using the Thermo Scientific FLASH 2000 Analyzer.

Table XI. Nitrogen content of fuel samples analyzed with modified Kjeldahl method and Thermo Scientific FLASH 2000 Organic Element Analyzer. Data from **Paper IV**.

| Fuel samples | Kjeldahl | FLASH 2000 | |
|--------------|---------------|---------------|------|
| | N (wt-% d.s.) | N (wt-% d.s.) | |
| | avg | avg | stdv |
| Bark | 0.40 | 0.32 | 0.02 |
| Peat | 2.06 | 2.03 | 0.06 |
| Coal | 1.80 | 1.81 | 0.04 |

The salts tested in the experiments were K_2CO_3 , K_2SO_4 , KCl , Na_2CO_3 , and $CaCO_3$. A portion of the char nitrogen was converted to cyanate in fuels loaded with K_2CO_3 , K_2SO_4 , and Na_2CO_3 , while the unloaded fuels and fuels loaded with KCl and $CaCO_3$ did not result in cyanate formation. Table XII shows the different fuels loaded with different levels of catalytically active alkali metal salts and the nitrogen content before and after the initial pyrolysis.

Table XII. Alkali metal loading of different fuels and the nitrogen content of the alkali metal loaded fuels before and after initial pyrolysis. (* calculated based on fuel nitrogen content analyzed with FLASH 2000, Table XI, and salt addition). Data from **Paper IV**.

| Fuel | Alkali metal loading | | FLASH 2000 | | |
|------|----------------------|---------------------------------|----------------------|------------------------|------|
| | wt -% | salt | Initial N content* | N after 10 s pyrolysis | |
| | | | N (wt-% d.s.) avg | avg | stdv |
| Peat | 1 | K ₂ CO ₃ | 2.00 | 2.42 | 0.03 |
| Peat | 5 | K ₂ CO ₃ | 1.85 | 1.91 | 0.05 |
| Peat | 10 | K ₂ CO ₃ | 1.68 | 1.64 | 0.05 |
| Peat | 15 | K ₂ CO ₃ | 1.38 | 1.13 | 0.03 |
| Peat | 10 | K ₂ SO ₄ | 1.76 | 1.76 | 0.02 |
| Peat | 10 | Na ₂ CO ₃ | 1.58 | 1.35 | 0.03 |
| Bark | 10 | K ₂ CO ₃ | 0.26 | 0.22 | 0.02 |
| Coal | 10 | K ₂ CO ₃ | 1.49 | 1.41 | 0.10 |

* calculated based on fuel N content analyzed with FLASH 2000 and salt addition

Char nitrogen to cyanate conversion during gasification (900°C 13% CO₂ in N₂) for peat loaded with different salts, but all containing 10 wt% alkali metal, is shown in Figure 27. Both potassium carbonate and sodium carbonate promoted char nitrogen to cyanate conversion, and the maximum for both salts occurred when roughly 50-60% of the char was converted. The maximum conversion was slightly higher for potassium carbonate than for sodium carbonate. A 10 wt% potassium carbonate loading corresponds to a 2.6 mol K/kg of loaded fuel, and a 10 wt% sodium carbonate to a 4.3 mol Na/kg of loaded fuel. A previous study by Kapteijn et al. [27] showed that the potassium carbonate is a more active catalyst than sodium carbonate, and also stated that if the reactivity of the alkali metal ions increases with the periodical order. It would appear that increase in alkali metal cation size would increase the reactivity of the oxidation reduction reaction occurring on the catalyst surface with CO₂. The reactivity of the catalyst is also affected by the surface area, pore structure, ash content, and how well the catalyst is dispersed on the char surface.

Potassium sulfate also acted as a catalyst in char nitrogen to cyanate conversion, but it was not as active as potassium or sodium carbonate. The maximum char nitrogen to cyanate conversion with K_2SO_4 occurred when more than 90% of the char has been consumed. In a previous study, Lee et al. [112] observed a lower catalytic activity of potassium sulfate compared to potassium carbonate during char conversion. Lang [111] stated in his study on the anion effects in alkali-catalyzed steam gasification that alkali salts from weak-acids are better catalysts than alkali salts from strong acids, sulfates having being slightly better catalysts compared to chlorides. He also stated that some sulfates can under gasifying conditions be reduced to weak acid sulfide form, which is an exceptionally good catalyst.

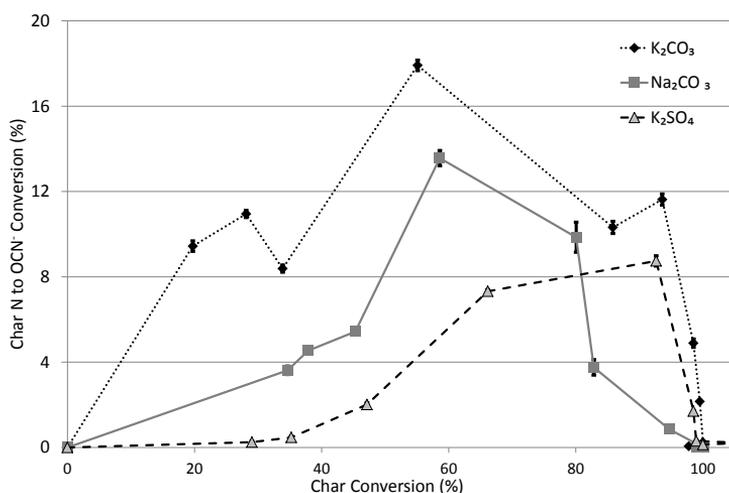


Figure 27. Char nitrogen to cyanate conversion versus char conversion during gasification (900°C 13% CO_2 in N_2) for peat loaded with 10 wt% alkali metals originating from different salts. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper IV**.

The impact of different levels of alkali metal loading on cyanate formation is shown in Figure 28. Char nitrogen to cyanate conversion for the 1 wt% K_2CO_3 loaded peat was almost nonexistent, and for the 5 wt% K_2CO_3 loaded peat, less

than 5% of the char nitrogen was converted to cyanate. A blank test conducted with unloaded peat did not show any cyanate formation. For the 10 wt% and 15 wt% loaded peat samples, the maximum conversion occurred at 50-60% char conversion. Roughly 17% of the char nitrogen was converted to cyanate of the 10 wt% loaded peat sample. A 5 wt% increase in the loading increased the char nitrogen to cyanate conversion to roughly 30%. The subsequent decrease in cyanate concentration seen in Figure 27 and Figure 28 is probably due to thermal decomposition [36].

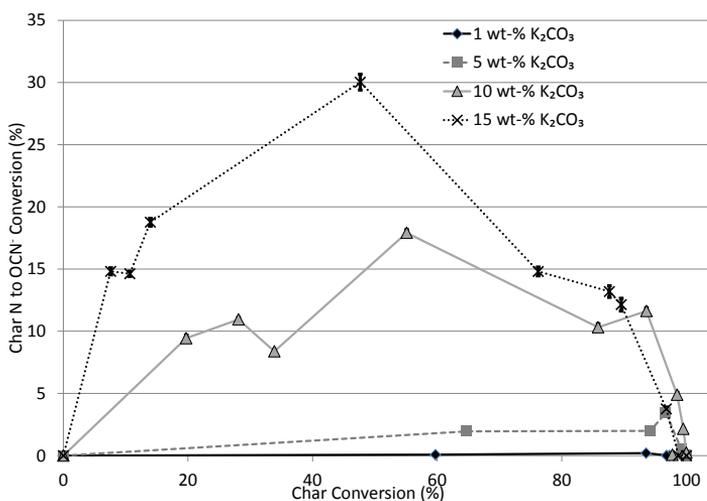


Figure 28. Char nitrogen to cyanate conversion versus char conversion during gasification (900°C 13% CO₂ in N₂) for peat loaded with different levels of potassium carbonate. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper IV**.

These results indicate that cyanate is formed via reactions involving char nitrogen and an alkali metal salt containing two alkali metal cations. Based on the catalytic gasification mechanisms proposed by Sams and Shadman [29] presented earlier in section 1.3, it is now proposed that K₂CO₃ reacts with a C-N site on the char, forming potassium cyanate, KOCN (**VIII**), and fully-oxidized reactive potassium intermediate (-CO₂K). The other possible mechanism is that

the fully-oxidized intermediate ($-\text{CO}_2\text{K}$) reacts with a C-N site, forming KOCN and gaseous CO (IX).

Possible mechanisms for cyanate formation with carbonates:

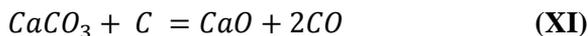


During gasification of K_2SO_4 loaded peat, a release of sulfur was detected. This indicates that K_2SO_4 reacts with the char resulting in sulfur release. The ratio between cyanate formation and the sulfur released was 2.6 to 1. Based on the cyanate formation and sulfur release the global reaction for potassium sulfate catalyzed cyanate formation was assumed to be:



The exact mechanisms behind cyanate formation with K_2SO_4 are partly unknown and needs to be studied further. Based on the work of Lang [111] one possibility is that K_2SO_4 first is reduced to K_2S and then in the presence of CO_2 it forms potassium carbon complexes and S is released as SO_2 .

CaCO_3 and KCl did not result in char nitrogen to cyanate conversion. According to McKee [16] CaCO_3 follows a different mechanism than alkali metal carbonates in catalytic gasification with CO_2 :



The difference in mechanism could be one reason why no cyanate was formed. The other reason is that calcium cyanate is in the form of $\text{Ca}(\text{OCN})_2$, this would imply that in order for calcium cyanate to be formed two nitrogen compounds should be located relatively close to each other in the char matrix. In order to determine why KCl did not form any cyanate needs to be studied further, e.g.

does alkali metal salts containing only one cation follow the similar gasification mechanisms as alkali metal salts containing two cations.

The effect of temperature on cyanate formation is shown in Figure 29. The maximum char conversion during the 900°C experiment occurred when just less than 60% of the char was converted, while for the 1000°C experiment, it occurred when roughly 75% of the char was converted. Based on the shape of the curve for the 1000°C experiment, it is entirely possible that the real maximum conversion occurs between 50-75% char conversion. It is also entirely possible that the real maximum conversion during the 900°C experiment was missed because only one data point was obtained between 35% and 87% char conversion. More intermediate levels of char conversion were obtained during the 800°C experiment because the rate of the gasification was slower at 800°C than at higher temperatures. The maximum char nitrogen to cyanate conversion during the 800°C experiment was obtained when almost all of the char was consumed. The maximum conversions for all the experiments occurred within 2%-units of one another. At higher temperatures the char conversion was expected to be faster thus also the fuel nitrogen to cyanate conversion would be faster. The first four data points for all of the experiments shown in Figure 29 were obtained after 10 s, 20 s, 30 s and 60 s exposure time. The char conversion was thus faster at higher temperature, except in for a few data points in the beginning of the 800°C and 900°C experiments. It was also expected that more char nitrogen would be converted to cyanate at higher temperatures but this was not the case. The reason for this was thought that at higher temperatures cyanate was both formed and decomposed, and also more nitrogen was assumed to be volatilized which would lower the nitrogen content in the char. The decrease in the cyanate concentration at the end of the 800°C experiment was a surprise as previous studies have showed that cyanate should be stable at temperatures below 850°C [36, 71].

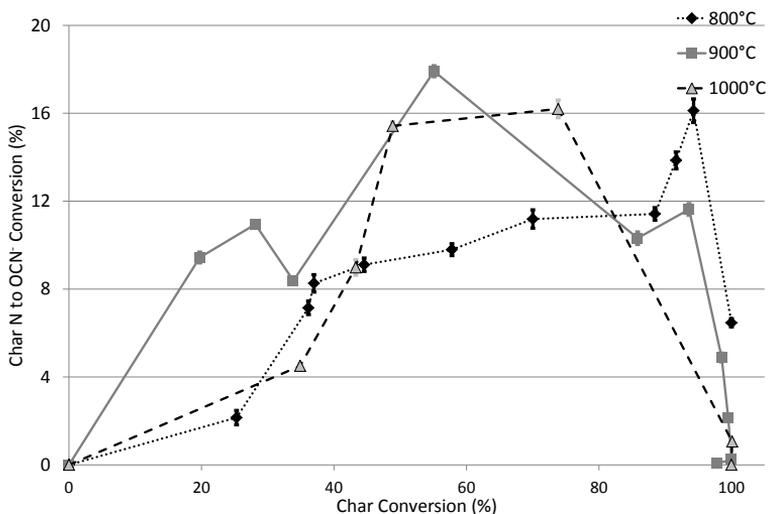


Figure 29. Char nitrogen to cyanate conversion versus char conversion during gasification (13% CO₂ in N₂) of 10 wt% K₂CO₃ loaded peat at different temperatures. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper IV**.

The impact of fuel on char nitrogen to cyanate conversion is shown in Figure 30. The potassium carbonate loaded bark and peat chars had almost identical patterns for the char nitrogen to cyanate conversion. The maximum conversion for both fuels occurs when just less than 60% of the char was converted, and the conversion was slightly higher for peat than for bark. For alkali metal loaded coal, the maximum conversion occurred when roughly 50% of the char was converted and was much lower than for peat and bark. Previous studies showed that during thermal treatment of peat and biomass the form of nitrogen containing compounds were rearranged. The share of amino and amide structures decreased, and the share of cyclic nitrogen-containing compounds increased during thermal treatment. The majority of the nitrogen compounds were still found in amide-containing structures, which were found to be relatively stable against thermal degradation [43, 113]. Even before thermal treatment the majority of fuel nitrogen in coal is in the form of heterocyclic compounds [45, 46]. This would indicate that nitrogen compounds found in non-

cyclic nitrogen compounds are more easily converted to cyanate than cyclic nitrogen compounds.

The calculated potassium to nitrogen molar ratio in the alkali metal loaded fuels prior to catalyst was 2.1 for peat, 2.4 for coal, and 13.6 for bark. The high value of bark is due to its low nitrogen content. This indicates that the form of nitrogen affects the char nitrogen to cyanate conversion, while the molar ratio of K:N does not affect the char nitrogen to cyanate conversion.

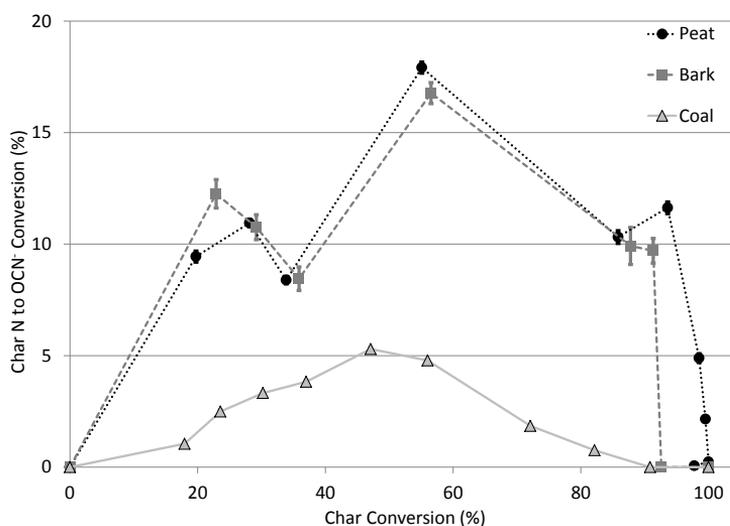


Figure 30. Char nitrogen to cyanate conversion versus char conversion during gasification (900°C 13% CO₂ in N₂) for different fuels loaded with 10 wt% potassium carbonate. Error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figure from **Paper IV**.

These results showed that the type and amount of alkali metal loading, and the form of organic nitrogen in the char, are the most important variables in char nitrogen to cyanate conversion. The effect of temperature had no clear impact on char nitrogen to cyanate conversion. During this work, the effect of CO₂ concentration in the surrounding atmosphere on char nitrogen to cyanate conversion was not studied.

After publishing the alkali doped results we looked at sodium cyanate decomposition in quartz glass holders. I noted that cyanate reacted with the sample holder. Due to the observed decomposition of the sodium cyanate with quartz glass the results were not published. The decomposition of cyanate in the alkali metal loaded fuel experiments before full char gasification may be due to reaction of cyanate with the quartz glass, and also could be the cause for the dips in the cyanate formation curves seen in some of the figures.

4.3.3 Cyanate formation and decomposition during thermal conversion of black liquor.

4.3.3.1 Cyanate formation

This part will focus on the formation of smelt cyanate, although in some Figures also show smelt cyanate decomposition. The decomposition is discussed in more detail in the next section. The nitrogen content of the liquor samples was determined with the modified Kjeldahl method. The hardwood black liquor had a nitrogen content of 0.087 wt% and the softwood 0.066 wt% on a dry solids basis. Fuel nitrogen to cyanate conversion and char yield of the hardwood black liquor during pyrolysis is shown in Figure 31, and of the softwood black liquor in Figure 32. For both liquors, over 20% of the fuel nitrogen during the 1000°C pyrolysis experiments and roughly 10-15% during the 900°C pyrolysis experiments were rapidly converted to cyanate. This was due to the catalytic reaction between alkali metal carbonate and nitrogen in the fuel. At higher temperatures, the cyanate both forms and decomposes; however, this was not the case at 800°C. The average smelt yield for black liquor is roughly 45-50% of black liquor dry solids [21]. The figures illustrate that at higher temperatures (900°C and 1000°C), all of the organic material was consumed and only the inorganic material remained. The final yield of both liquors at 900°C and 1000°C was below 40 wt%, which would indicate that alkali metals were also volatilized. When the pyrolysis was conducted at 800°C the final yield was just less than 60 wt%, which means that the residue consisted of both fixed carbon and inorganic material.

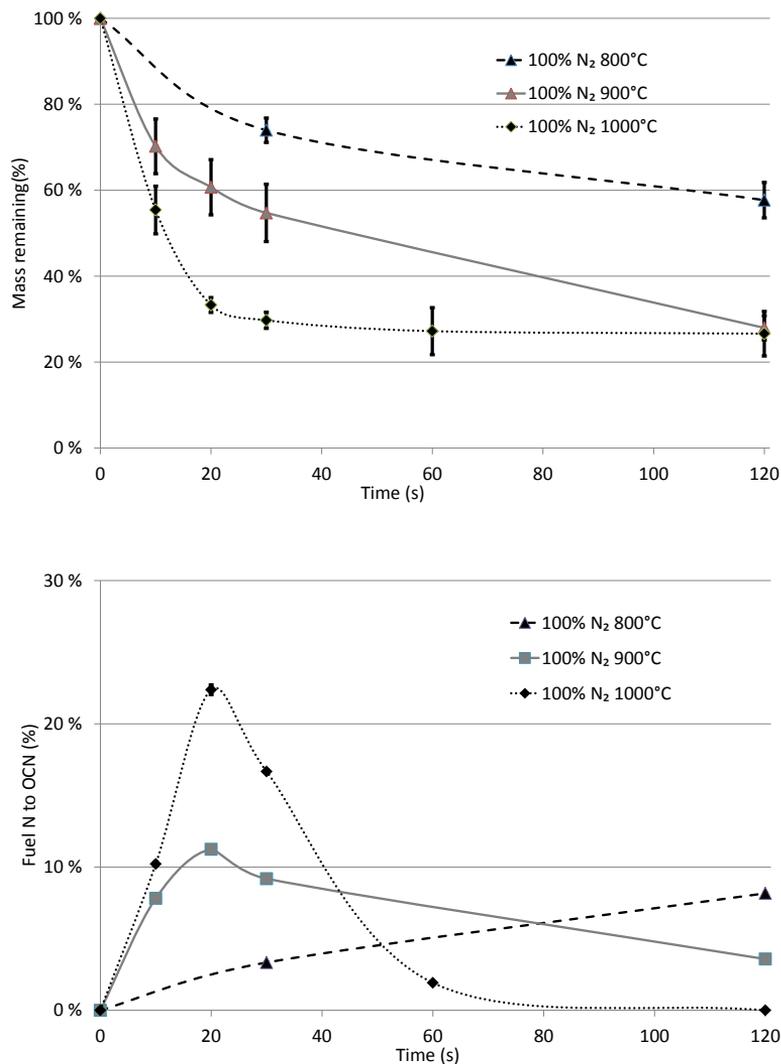


Figure 31. Char yield (top) and fuel nitrogen to cyanate (bottom) conversions of hardwood black liquor pyrolyzed in nitrogen at different temperatures. Error bars in the char yield figure (top) represent the standard deviations of six weighed chars, and in the fuel nitrogen to cyanate figure (bottom), the error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figures from **Paper V**.

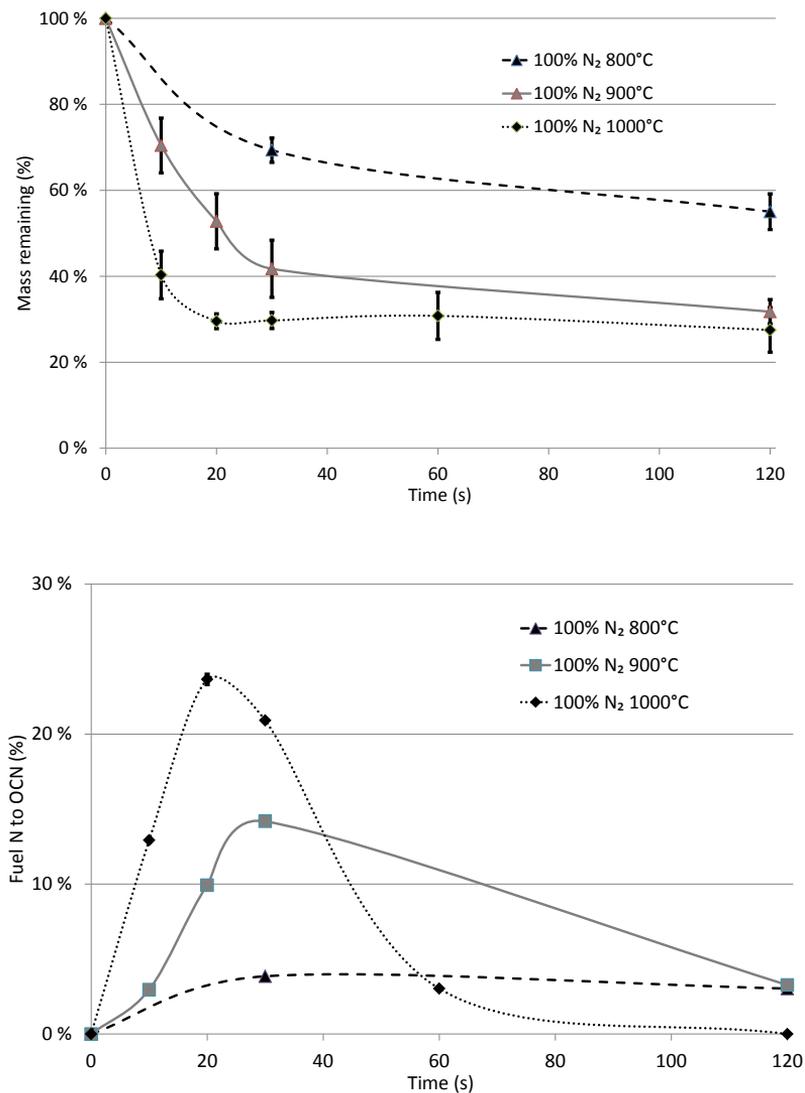


Figure 32. Char yield (top) and fuel nitrogen to cyanate (bottom) conversions of softwood black liquor pyrolyzed in nitrogen at different temperatures. Error bars in the char yield figure (top) represent the standard deviations of six weighed chars, and in the fuel nitrogen to cyanate figure (bottom), the error bars represent the standard deviations of six ion chromatography analyses conducted on one solution. Figures from **Paper V**.

The cyanate formation during gasification experiments were conducted by first pyrolyzing the black liquors for 30 seconds at 800°C to form a char. After the 30 seconds, the pyrolysis hardwood liquor char yield was 74% and roughly 3.3% of the fuel nitrogen was converted to cyanate. The char yield for the softwood liquor was 69% and 3.9% of the fuel nitrogen was converted to cyanate during the initial pyrolysis. The formed chars were gasified at 800-900°C in 13-50% CO₂ atmosphere using N₂ as the balance gas. Figure 33 shows the fuel nitrogen to cyanate conversion during gasification of the pyrolyzed chars. The black markers in Figure 33 represent the softwood black liquor and the grey markers the hardwood black liquor. After complete gasification a smelt remained, which averaged for each gasification experiment 45 wt% for the softwood black liquor and 47 wt% for the hardwood black liquor. Full conversion of black liquor to smelt was obtained after roughly two minutes of gasification at 800°C and one minute of gasification at 900°C. The amount of cyanate found in hardwood smelt was slightly higher when the gasification was conducted at 900°C than at 800°C. This was not the case for the softwood smelt. No clear differences between fuel nitrogen to cyanate conversion were detected when the gasification was conducted at 800-900°C in 13-50% CO₂. Most of the cyanate was formed just at the end of the gasification when almost all of the char was converted. Cyanate formation at 1000°C 13% CO₂ in N₂ was also tested, but after just 10 seconds of exposure, almost all of the fixed carbon was volatilized. At this point roughly 20% of the fuel nitrogen was converted to cyanate, and after this point the cyanate content started to decrease due to thermal decomposition.

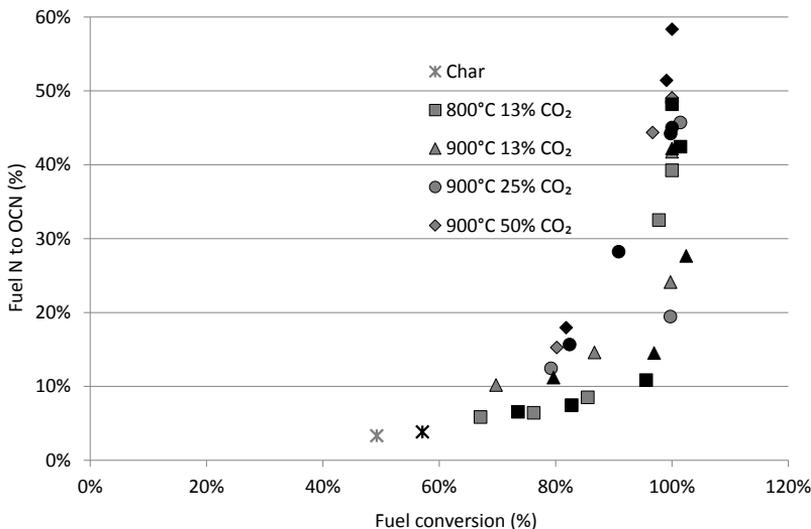


Figure 33. Fuel nitrogen to cyanate conversion during gasification of hardwood and softwood chars at 800°C and 900°C at different concentrations of CO₂. The black markers represent softwood black liquor and the grey markers represent hardwood black liquor. Data from **Paper V**.

The share of fuel nitrogen converted to NO during char gasification is shown in Figure 34. Less than 5% of fuel nitrogen was released as NO during char gasification. For both liquors, the share of NO formed decreased with increasing CO₂ concentration. More NO was formed when the gasification was conducted at 900°C in 13% CO₂ in N₂ than at 800°C in 13% CO₂ in N₂. The low amount of formed NO can originate from either char nitrogen or from decomposition of cyanate.

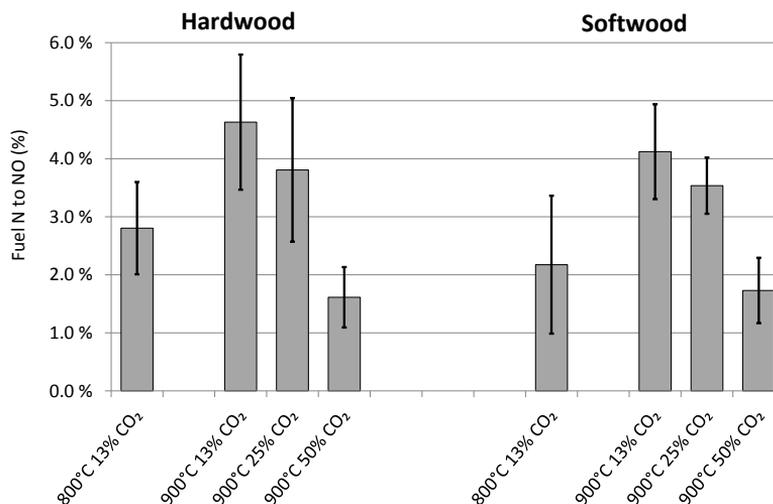


Figure 34. Fuel nitrogen to NO conversion during gasification of black liquor chars at different temperatures and atmospheres. Figure from **Paper V**.

4.3.3.2 Cyanate decomposition

The stability of cyanate in 13% CO₂ atmosphere was tested by gasifying black liquor hardwood droplets (10±0.5 mg) for different times at 800°C and 900°C, Figure 35. At 800°C 13% CO₂ in N₂ the smelt was obtained after 180 seconds of gasification, and at 900°C 13% CO₂ in N₂ it was obtained after 60 seconds. The cyanate in smelt was stable at 800°C, while it decomposed at 900°C. The stability of cyanate below 850°C in CO₂-containing atmospheres has also been previously reported [36]. Based on these findings, it was determined that during the 800°C experiments the black liquor droplets were gasified first for 180 seconds in 13% CO₂ and during the 900°C experiments for 60 seconds to obtain a smelt after which the gas composition inside the reactor was switched in order to obtain data on cyanate decomposition in different atmospheres. These points represent the time at 0 seconds for the upcoming decomposition figures. Roughly 51% of the black liquor nitrogen was converted to cyanate after 180 seconds of gasification at 800°C 13% CO₂, and roughly 48% when the black liquor was gasified for 60 seconds at 900°C 13% CO₂.

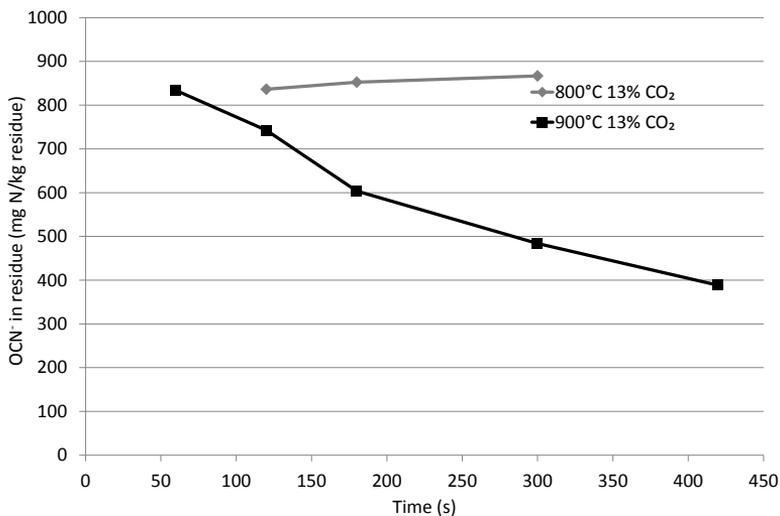


Figure 35. Stability of cyanate in 13% CO₂ atmosphere. Data from **Paper IV**.

Figure 36 shows the decomposition of cyanate after the gas composition was changed from 13% CO₂ to 3% O₂ or 100% N₂ at 800°C and 900°C. The decomposition was faster in oxidizing conditions than in inert, and the decomposition was faster at higher temperatures. In oxidizing conditions, at both temperatures, all of the cyanate in the smelt was decomposed or oxidized in just under 2 minutes. After 5 minutes of exposure in inert conditions at 800°C, only about 40% of the cyanate was decomposed, and at 900°C after 7 minutes of exposure, about 75% of the cyanate was decomposed.

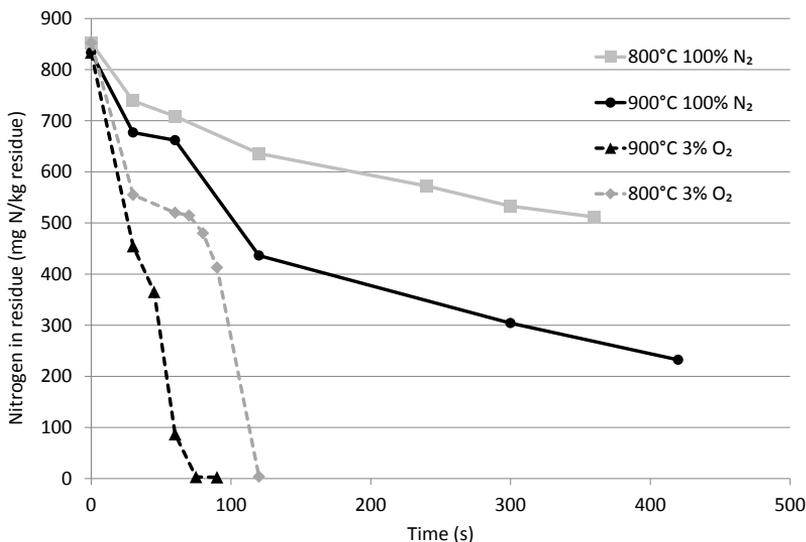


Figure 36. Cyanate decomposition in 100% N₂ and 3% O₂ in N₂ at 800°C and 900°C. Data from **Paper V**.

The impact of gas composition in the decomposition of cyanate at 900°C is shown in Figure 37. At 900°C the decomposition of cyanate was slowest in the atmosphere that consisted of CO₂ and N₂. The decomposition of cyanate was slightly slower at 26% CO₂ in N₂ than at 13% CO₂ in N₂. In inert conditions (100% N₂) the decomposition was slightly faster than in the CO₂ containing atmosphere. The decomposition of cyanate was quickest in 3% O₂ / 97% N₂. The decomposition of cyanate in 13% CO₂ / 3% O₂ / 84% N₂ atmosphere was slower than in the atmosphere containing only oxygen and nitrogen. During cyanate oxidation, CO₂ was produced. The atmosphere already contained 13% CO₂, which may be the cause for the oxidation reaction to slow down. This would indicate that a further increase in the CO₂ concentration in O₂ and N₂ containing atmosphere would slow the decomposition even more.

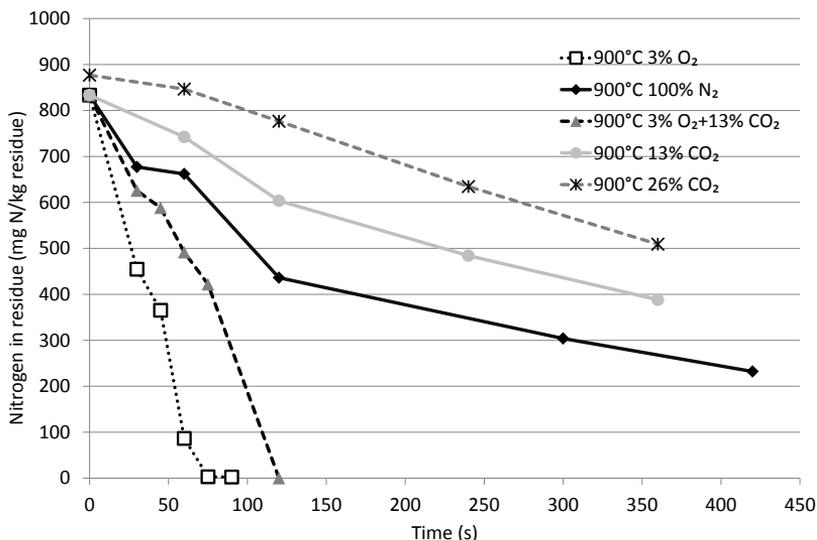


Figure 37. Cyanate decomposition at 900°C in different gas compositions. Figure from **Paper V**.

The share of NO formed during cyanate decomposition was slightly higher during the 900°C experiments compared to the 800°C experiments, Figure 38. Slightly more NO was formed in oxygen-containing atmospheres than in inert conditions. Roughly 25% of the cyanate still remained in the residue after the decomposition at 900°C in the inert atmosphere, and more than 60% remained at 800°C in the inert atmosphere. It was concluded that around 50% of the initial black liquor nitrogen remained in the formed smelt droplet prior to the decomposition. The weight of the smelt droplet prior to the decomposition experiments was roughly 4 mg, meaning it contained 0.003-0.004 mg of nitrogen. The low nitrogen content in the smelt combined with background noise from the analyzer made it difficult to measure the amount of NO formed.

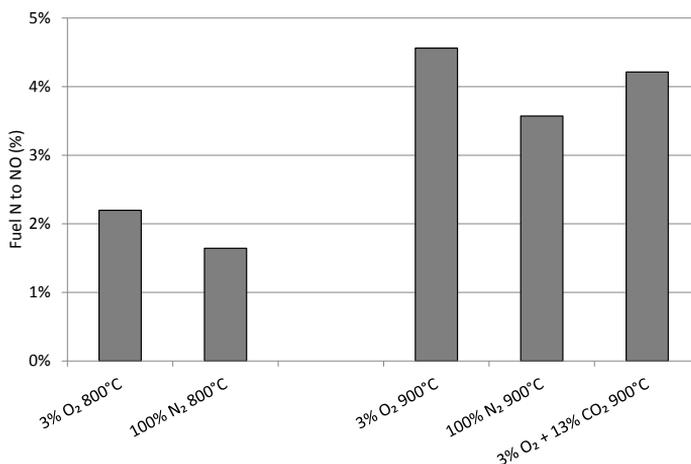


Figure 38. Share of the initial fuel nitrogen converted to NO during cyanate decomposition. Data from **Paper V**.

Zhu [114] studied the decomposition of pure sodium cyanate salt in a TGA. Based on the final weight, at temperatures below 800°C, pure sodium cyanate appears to react with oxygen to form sodium carbonate and volatile products according to reaction **(XIII)**.



Zhu also found that in inert conditions (100% N₂) the weight loss was constant indicating thermal decomposition of sodium cyanate, but what compounds were formed and released is unknown.

This work looked at the influence of temperature and gas composition on cyanate decomposition in smelt. Because the concentration of cyanate in smelt is so low, it was not possible to determine what solid products were formed. The only gaseous N species monitored was NO, but these important results show little NO is formed from cyanate decomposition, even in oxidizing conditions. This data provided important new information that will allow for follow up studies to clarify important open questions such as the reason for the inhibiting effect of CO₂ and the form of released char N.

5 CONCLUSIONS AND FUTURE RESEARCH

5.1 Conclusions of this work

The fate of nitrogen in modified black liquors was studied in the first part of this work. This led to new insights into cyanate formation and thus, cyanate formation and decomposition became the focus of rest of this thesis work. The fate of modified black liquor nitrogen was studied in both a mill-scale sampling campaign and in laboratory experiments. NO formation, cyanate formation during thermal conversion of black liquor, cyanate formation during gasification of fuels loaded with alkali metal salts, and the decomposition of smelt cyanate were all studied in laboratory-scale experiments.

The mill-scale camping shows that the addition of biosludge increased the nitrogen content of the black liquor. Biosludge does not result in higher NO formation in the recovery boiler, but can result in more cyanate in the smelt. Green liquor samples from the mill and laboratory made smelts both shows that the biosludge addition will most likely increase the nitrogen content in the smelt, where it is in the form of cyanate. The cyanate forms NH_3 during green liquor handling and white liquor preparation, and an increase in cyanate can increase the nitrogen emissions from the rest of the recovery cycle depending where the non-condensable gases and methanol are burned.

The laboratory scale experiments show that in most cases the NO and cyanate formation slightly decreases with lignin removal. The removal of lignin from black liquor at a pulp mill would thus mean that less NO is formed per ton of pulp produced. The addition of biomass to black liquor increased both the NO and cyanate formation of the mixture compare to original black liquor. The results indicated that black liquor acts a catalyst and converts portion of the mixed biomasses nitrogen to cyanate. This discovery led to that a more detailed study of cyanate formation and decomposition. The addition of a fuel, which has a higher nitrogen content than black liquor, could affect the NO and cyanate formation in a recovery boiler.

Black liquor char contains high levels of sodium carbonate and we speculated that it was reactions between sodium carbonate and char-N that were responsible for cyanate formation. This hypothesis was tested by adding different alkali metal and earth alkali metal salts to different fuels. The loaded fuels were then gasified and analyzed if cyanate was formed. The study shows that K_2CO_3 , Na_2CO_3 , and K_2SO_4 result in cyanate formation from char-N, while KCl and $CaCO_3$ do not. The form of the organic nitrogen in the fuel also appears to affect the cyanate formation. Nitrogen in non-cyclic compounds appeared to be more easily converted to cyanate than nitrogen in cyclic compounds. These results suggest that during large scale catalytic (with alkali metal carbonates as catalyst) gasification of fuels to syngas a portion of the fuel nitrogen would be converted to the inorganic form cyanate, which could remain in the inorganic residue.

Based on the work with alkali metal loaded fuels it is now known that cyanate formation during thermal conversion of black liquor is caused by the reaction between black liquor char nitrogen and alkali metal carbonates, which are formed during pyrolysis. Before this work the mechanisms behind cyanate formation during thermal conversion of black liquor were unknown.

The parameters affecting cyanate formation and decomposition during thermal conversion of black liquor were studied in detail. The experiments show that a portion of black liquor nitrogen is converted to cyanate during the pyrolysis phase, but quickly decomposes when the temperature is higher than $900^\circ C$. During gasification of black liquor char most of the char nitrogen is converted to cyanate and less than 5% of fuel nitrogen is converted to NO during char gasification, this result corresponds with previous studies.

Smelt cyanate is stable in CO_2 containing atmosphere at temperatures below $900^\circ C$, and decomposes slowly in higher temperatures. The gas composition and temperature are the key factors in smelt cyanate decomposition. Decomposition is faster in oxidizing conditions than inert conditions and faster at higher temperatures. More experimental work needs to be conducted with different gas composition and temperatures to obtain more data so the decomposition of

cyanate as a function of temperature and gas composition can be modelled accurately. The study also shows that only a small portion of cyanate decomposes to form NO. This information regarding cyanate formation and decomposition will provide new information for recover boiler operators, which they can utilize to minimize the NO and cyanate formation in the recovery boiler.

One object of this work was to further clarify the fate of black liquor nitrogen during thermal conversion, especially the formation and decomposition of cyanate. In the future this data would be used in CFD modelling, which would more accurately describe the fate of black liquor nitrogen in the recovery boiler. The major pathways of nitrogen during thermal conversion of black liquor are shown in Figure 39. The term α_1 represents the share of black liquor nitrogen forming volatile nitrogen products during pyrolysis, and the rest $(1-\alpha_1)$ remains in the char. This work clearly shows that modification of black liquor will affect the nitrogen content of black liquor, which will affect the amount of volatile and char nitrogen.

During char conversion most of the char nitrogen will end up in the smelt as cyanate. Less than 5% of the initial black liquor nitrogen is converted to NO during char conversion; this is roughly 10% of the char nitrogen.

In inert conditions (100% N₂), fixed carbon is oxidized with alkali metal carbonate and sulfate to volatile products. Small amounts of cyanate are formed during pyrolysis due to the reactions between alkali metal salts and black liquor nitrogen. At higher temperatures such as 900 or 1000 °C, where the char carbon can be completely gasified by the oxygen in sulfate and carbonate, more cyanate can be formed.

In an earlier modeling approach, all of the nitrogen in carry-over particles is assumed to be oxidized to NO [115]. The amount of cyanate in the smelt bed will depend on spraying conditions, whether the droplets burn in flight, burn on the wall or burn on the char bed because of the gas atmosphere that the cyanate

is exposed to. The lower furnace temperature and the gas composition are the most important parameters in minimizing the cyanate flowing out with the smelt. Higher temperatures in the lower furnace will increase the rate of cyanate decomposition without large increases in NO in the lower furnace. Cyanate decomposes in inert and oxygen-containing atmospheres, while CO₂ in the atmosphere reduced the rate of decomposition.

This work provided new knowledge regarding the formation of cyanate during thermal conversion of black liquor. Recovery boiler owners and operators can utilize the results presented in this work to estimate the impact of black liquor modification on recovery boiler operations and how to better control NO formation during combustion and the amount of cyanate exiting the recovery boiler.

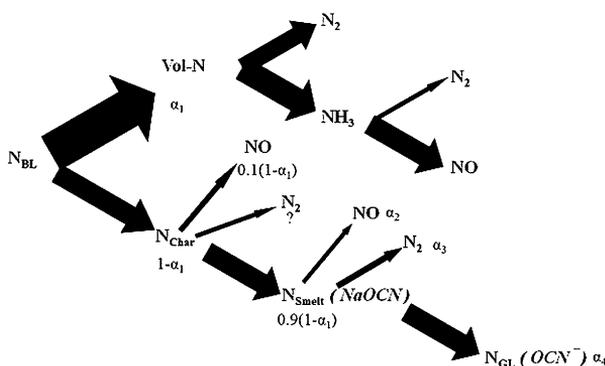


Figure 39. Fate of nitrogen during thermal conversion of black liquor.

5.2 Future work

The disposal of biosludge by burning it with black liquor is well-established in Finland. The removal of lignin is currently being implemented and will grow as soon as more high-value uses for lignin are available. There are no plans at the moment to mix biomass residue with black liquor and co-fire the mixture in a recovery boiler.

In order to clearly determine the impact of lignin removal from black liquor on chemical recovery, measurement campaigns should be conducted at mills that are firing modified black liquors. Important variables that need to be studied are: NO and cyanate formation; sheet breakup and black liquor droplet formation; carry-over formation and composition; and the flow of non-process inorganic species in the recovery cycle. The sulfur release during combustion of reduced lignin liquors should also be studied.

At the laboratory scale, more experimental work should be conducted to clearly identify the mechanisms behind cyanate formation and to determine which nitrogen compounds form cyanate during thermal conversion of alkali salt loaded fuels. This could be conducted by using model compounds as fuels or by identifying nitrogen containing compounds in chars from different fuels. Also the influence of CO₂, H₂O and SO₂ concentrations in the gasification atmosphere on cyanate formation with alkali salt loaded fuels should be studied more. This work would provide new information to help clarify the fate of fuel nitrogen during catalytic gasification with alkali metal carbonates and sulfates as catalyst. It would also give deeper understanding into the reasons for black liquor cyanate formation.

The setup used in this work is designed to describe reactions in carry-over droplets. In the current setup, the smelt droplets are exposed from all directions to the surrounding atmosphere; this might not give accurate kinetics for cyanate decomposition in the smelt bed. In the smelt bed, the smelt is exposed from only one direction to the surrounding atmosphere. In addition, the flow of formed gases out from the smelt is possible in only one direction, while formed gases from smelt droplets can flow in several directions. Different setups should be tested in order to provide accurate data for cyanate decomposition in a smelt bed. More experimental work needs to be conducted in order to obtain rate expressions for cyanate formation and decomposition in different gas compositions. Experiments should be conducted in temperature range of 1000-1200°C and also in gas composition containing different mixing ratios of CO₂, H₂O, N₂ and O₂ as these compounds typical found in flue gases. In this work

only the decomposition of cyanate to NO was measured the rest was assumed to form N₂. More experimental work is needed to determine what nitrogen compounds are formed during decomposition of the cyanate. In the future, this data should be implemented in a simplified droplet CFD model so that the fate of black liquor nitrogen inside the recovery boiler can be predicted with more confidence that the most important variables are captured in the model. This would help companies and researchers develop strategies to further decrease NO emissions without the addition of flue gas treatment technologies.

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