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Influence of biomass pre-treatments on the formation of NO and NO-precursors in the different combustion stages

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Abstract

In this thesis, the influence of pre-treatments on biomass combustion has been investigated. The main object was to clarify how those pre-treatments affect NO emissions and the formation of NO-precursors.

The pre-treatments which have been investigated are steam explosion, torrefaction and a combination of washing and torrefaction. The investigated biomasses were spruce bark and wheat straw.

Single particles of the investigated biomasses were combusted in a quartz glass single particle reactor. The total NO emissions were calculated based on measured NO concentrations as a function of time and flow of the combustion air.

An additional set-up has been applied to the single particle reactor to investigate the formation of NH_3 during pyrolysis of the biomasses. Wet chemistry methods have been used to quantify NH_3.

Keywords: Biomass, Combustion, Pyrolysis, NO, NH_3, Pre-treatment

Förord

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Table of Contents

1. Introduction

Biomass has been the most important energy source in history of humankind. However, when the industrial revolution started, fossil fuels became increasingly important to cover the rising energy demand. Nowadays, the trend is going again in the other direction as biomass has been increasingly used the last decades [1]. This trend can mainly be explained by environmental and economic reasons [2]. Fossil fuels are non-sustainable energy sources, which have a negative impact on the environment due to emissions of greenhouse gases such as CO_2. The intensive use of fossil fuels since the industrial revolution caused a rapid increase of the CO_2 concentration in the atmosphere which is still ongoing. CO_2 is also released during the combustion of biomasses. However, in general biomass can be seen as a CO_2-neutral energy source. The amount of carbon emitted from biomass is approximately the same as the amount that will be absorbed from the atmosphere by growth of new plants [2].

The development and application of new technologies during the last decades also made the use of biomass interesting from an economical point of view. Lower costs and high availability in many countries make biomass competitive with fossil fuels and can secure energy supplies [2]. Furthermore, new legislations require increasing use of sustainable energy sources such as many biomasses. The European Union set the goal, that 27% of its total energy consumption in 2030 should be covered by renewable energy sources [3, 4] and greenhouse gases should be reduced by 40% as compared to 1990 [5]. Biomass is here the most important source. Nowadays 64% of the primary renewable energy production is generated by combustion of biomass [5].

Biomass combustion plays an important role in Finland as compared to many other countries. In 2017 37% of the total energy combustion (497 TJ) came from fossil fuels while the corresponding number was 45% in 2011 (618 TJ). During the same time the amount of energy produced from biomass increased from 22% (308,900 TJ) to 27% (361,432 TJ) [6]. In addition, the CO_2 emissions were reduced from 53 Mt to 41 Mt.

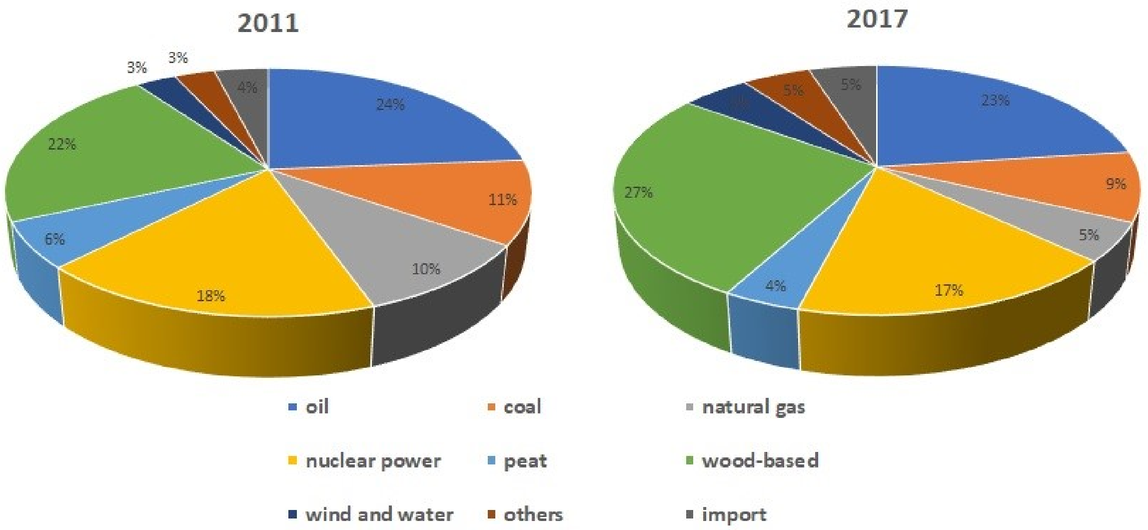

Fig. 1 Development of energy sources in Finland from 2011 to 2017 [6].

In spite of the potential of utilizing energy from biomass, there are many challenges that need to be considered. Biomass appears in various forms, and, as a result, systems which can handle many kinds of fuels are necessary. As with nearly all fuels, NO_x emissions are also of concern in the case with biomass, since the legislation is getting more stringent by time.

This thesis focuses primarily on the release and formation of NO and NH_3. NH_3 can serve as a precursor for NO_x-formation. The main objective was to clarify, how various pre-treatment methods, which can be used to improve different properties of biomass, affect the formation of NO and NH_3 during thermal conversion. The biomasses investigated were spruce bark and wheat straw. In addition, black liquor which is a waste material from the paper industry was investigated. Combustion experiments from pretreated biomasses and untreated biomasses were performed in a single particle reactor under well-controlled conditions.

2. Background

2.1 Biomass

Several definitions for biomass exist, but in general biomass can be defined as organic material that stems from plants [2]. Biomass can also be defined as organic matter which is derived from living organisms but also from recently living organisms [1]. Biomass is usually divided into four sub groups: woody plants, herbaceous plants, aquatic plants and manures [2]. The organic matter is produced by organisms which convert CO_2 to organic matter by photosynthesis using the energy from the incoming sunlight [2]. The process can be described by the general formula:

$$CO_2 + 2\,H_2A + h\nu \rightarrow (CH_2O)_n + H_2O + A_2 \qquad (1)$$

In this reaction A is an oxidizing agent. Most living forms use oxygen as an oxidizing agent. Some organisms, on the other hand, use sulfur as an oxidizing agent. The empirical formula CH_2O describes the smallest building unit for organic matter. In the plant the small building units form big macrostructures. The strongest polymer with a crystalline structure is cellulose which is built of glucose units. The hemicellulose has a random, amorphous structure since it is built up of a range of sugar molecules. The third important component is lignin which is an aromatic macropolymer. Crosslinking of lignin to other polymers results in strength in the cells of the plant [2]. Tab. 1 shows the share of the lignocellulosic constituents in bark and straw.

Tab.1 Lignocellulosic constituents of bark and straw [wt%] [7]

[wt%]	bark	straw
Hemicellulose	29.8	39.1
Cellulose	24.8	28.8
Lignin	43.8	18.6
Ash	1.6	13.5

In general, biomass does not only consist of organic material. Nutrients are absorbed during growth, especially Cl, N, P and S [8]. Other important constituents are also silica, alkali metals and some other metals. These may form ash during combustion and therefore it is important to consider biomass as an organic-inorganic product [9]. The amount of such ash-forming elements can vary significantly between various types of biomass as seen in tab. 1. The ash content and its composition are strongly influenced by the combustion behavior of the biomass, and depending on the ash quality, different challenges (e.g. corrosion, fouling, emissions, etc.) may arise during plant operation.

The two main methods for converting the energy bound to biomass are biochemical conversion, such as production of biogas, and thermochemical conversion. Fig. 2 presents a short overview of the possibilities for biochemical and thermochemical conversion. Thermochemical conversion, especially combustion, is the most applied technique. In combustion, heat is generated which can be applied for heating or for conversion of heat into electricity. Alternatively, gasification of biomass can be applied in order to produce alternative fuels and for recovering chemicals [7]. It is noteworthy that alternative fuels derived from biomasses are not entirely renewable energy sources due to the energy consumption of the production process [9]. Nevertheless, in multiple cases it is beneficial to convert biomass to fuels with a higher energy density. Biomass usually has a low energy density compared to other fuels [8]. In addition, in applications where liquid or gaseous fuels are needed, biomass is unsuitable and cannot be used as such.

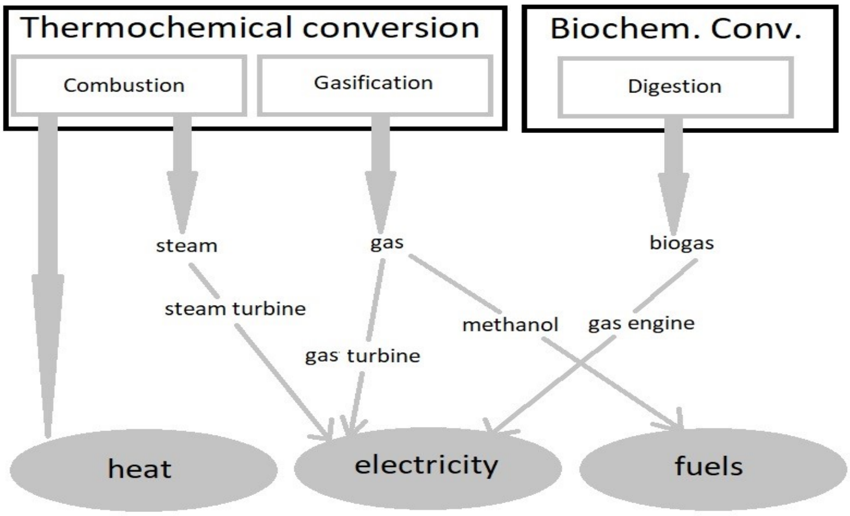

Fig. 2 Example of conversion methods for biomass [7].

2.2 Combustion and gasification of biomass

2.2.1 Combustion in fluidized bed boilers

Combustion of biomass is an essential source for primary energy production from renewable energy sources [5]. One favorable technique for combustion of biomass is fluidized bed combustion [10]. In a fluidized bed boiler, the fuel is fed to the reactor as small particles, usually of a size of around 0.1 – 10 mm. In the reactor, the fuel is mixed with particles of a bed material, which is usually quartz. This mixture of fuel and bed particles is brought to a fluidized state by blowing primary combustion air from the bottom of the reactor into the boiler. Hereby, two main types of fluidized bed boilers can be classified: the circulating fluidized bed (CFB) and the bubbling fluidized bed (BFB). The main difference between these two boiler types is the velocity of the primary air. Fig. 3 shows a schematic model of the two different boiler types. The velocity of the incoming combustion air is usually around 1-3 m/s in a BFB, depending on the size of the boiler [11]. The velocity is high enough to generate fluidization, but low enough to prevent entrainment of solid particles to the gas flow. In a circulating fluidized bed, the velocity is clearly higher, around 6-10 m/s [11]. At this velocity, the bed particles are carried out of the furnace. The particles which are leaving the furnace are then separated from the flue gas and collected in a cyclone and returned to the bed. Further details about differences of those boiler types will not be discussed in this thesis but can be found in the literature [11].

Fluidized bed boilers have several advantages compared to other combustion techniques. In general, fluidized boilers have a high flexibility of fuels and fuel mixtures. The utilization of small fuel particles enables good heat exchange as a result of the large solid-gas exchange area [11]. Furthermore, the temperature is distributed uniformly throughout the furnace. Hence, fluidized bed systems have a good combustion efficiency. Limitations with fluidized beds are for example utilization of fuels with low ah softening and melting points. This is of particular importance for biomasses since they usually contain significant amounts of alkali metals. Softened and molten ash causes challenges such as corrosion and agglomeration of the bed [12].

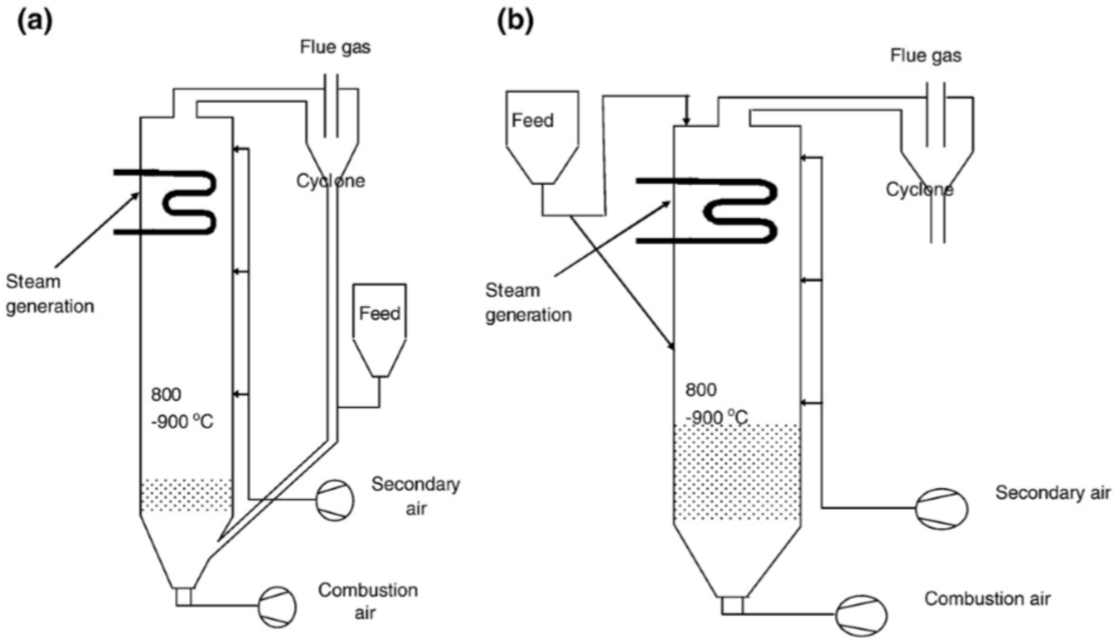

Fig. 3 A circulating fluidized bed boiler (a) and a bubbling fluidized bed boiler (b) [11].

The control of nitrogen containing gaseous emissions is also a challenge in fluidized bed boilers. Harmful emissions can vary significantly, depending on what type of fuel or mixture is fed to the boiler. During combustion of coal for example, significant quantities of nitrous oxide (N_2O), which is a 15 times more effective greenhouse gas than CO_2, are formed. In contrast, almost no N_2O is formed from biomass combustion [13]. Instead, a notable fraction of the fuel nitrogen is released as nitrogen oxides. Nitrogen oxides are often described with the formula NO_x. The major part is present as NO and only smaller amounts as NO_2 [12]. It is crucial to diminish those NO_x emissions as they are harmful to the environment. NO_x in the atmosphere leads to the formation of photochemical smog, increases ground level ozone and causes acid rain [14]. Different methods can be applied in fluidized bed boilers to decrease NO_x emissions: pre-combustion, combustion control and post-combustion techniques are the most common approaches [14]. Hitherto, selective catalytic reduction (SCR) is the most advanced and most effective post-combustion technique. Depending on the system, it is possible to reduce NO_x emissions by up to 90% [14]. The reduction reaction of NO can be expressed as follows:

$$4\,NO\,(g) + 4\,NH_3(g) + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (2)$$

2.2.2 Gasification

As mentioned in chapter 2.1, there are various ways to convert fuels thermochemically. One alternative besides combustion is gasification. In general, gasification is a process in which a solid or liquid carbonaceous material is converted into gaseous form [15, 16]. Gasification is often executed in a fluidized bed reactor. CFB technology has already been used for biomass gasification since the 1980's [17]. While the purpose with combustion is to achieve full oxidation of the fuel, the goal with gasification is to only partly oxidize the fuel [18, 19]. The main reactions during gasification are:

Partial oxidation:	$C + 0.5\,O_2 \rightarrow CO$	$\Delta H < 0$	(3)
Complete oxidation:	$C + O_2 \rightarrow CO_2$	$\Delta H < 0$	(4)
Water gas reaction:	$C + H_2O \rightarrow CO + H_2$	$\Delta H > 0$	(5)
Water gas shift:	$CO + H_2O \Leftrightarrow CO_2 + H_2$	$\Delta H < 0$	(6)
Methane formation:	$CO + 3\,H_2 \Leftrightarrow CH_4 + H_2O$	$\Delta H < 0$	(7)

The product from gasification is a gas mixture called syngas, which mainly contains CO, H_2, CO_2, CH_4 and N_2. Hydrogen is formed in the water gas reaction in which carbon is oxidized by steam to CO. The formed CO can further react with steam in the water gas shift reaction or form methane when reacting with hydrogen. The water gas reaction, in which the desired products CO and H_2 are formed, is an endothermic reaction which means that energy has to be supplied to favor this reaction. Hence, oxygen is added so that some carbon is oxidized to CO_2. The heat which is released from this reaction can be deployed by the endothermic water gas reaction [20]. The composition of this syngas is highly depending on the conditions during the gasification process. Gasification processes can be classified depending on the atmosphere in which the gasification takes place. In some processes atmospheric air is used. Other processes implement steam or different mixtures of steam and oxygen or steam and air [20]. Utilization of ordinary air gives a syngas with around 8-14 vol.-% hydrogen, hence with a relatively low heating value of only 4-6 MJ/m^3 [18, 20]. In processes in which pure oxygen and steam are utilized, the hydrogen content can be increased to up to 60 vol.-% resulting in higher heating values between 10-16 MJ/m^3 for the syngas. However, processes, in which pure oxygen is used, are much more energy demanding as additional set-ups for oxygen production are needed. Also, steam-blown gasification requires steam with high temperatures of around 700 °C which causes high energy consumption [20]. Recent research is focusing on the implementation of low-temperature steam for gasification via possible retrenchments in terms of energy consumption. However, experiments revealed that temperature is the most important parameter on how much hydrogen is formed [20]. Furthermore, the hydrogen yield is increasing when the steam/fuel-ratio is increased. Other factors than temperature and steam/fuel-ratio have only a minor influence on the hydrogen content of the syngas [20].

Despite many challenges, gasification of biomass is a promising technique. Combustion of biomass for example is limited to immobile applications. On the contrary, products from gasification can be stored and transported for further use [7, 19]. For instance, hydrogen can be separated from the syngas and can be used in fuel cells [21]. Further, the syngas can be applied to produce liquid hydrocarbon fuels or various other chemicals for example with the Fischer-Tropsch method. Even immobile power production gasification plants have advantages as compared to direct combustion plants, especially when impure and challenging fuels are used. Gasification enables the production of standardized gases of high quality which simplifies stable power production. The produced gases can be used for power production using power gas engines or gas turbines [19]. In terms of overall energy efficiency, gasification is in some cases the most appropriate method for converting biomass to energy. However, there are challenges that has to be dealt with in order to make gasification of biomass a widely used technology. Gasification of biomass is not as mature as the gasification of coal for instance [17]. A major challenge hereby is the purification of the syngas. As described in chapter 2.1, biomass contains a great variety of volatile elements. Hence, it is unavoidable that undesired impurities such as NH_3, H_2S, HCl, SO_2 and tars are present in product gases. Such impurities can cause problems in downstream applications [21]. The reducing conditions in gasification cause that the fuel bound nitrogen is partly converted into NH_3. Ammonia is a problematic impurity because it often acts as a catalyst poisoner in downstream applications. Furthermore, NH_3 can be oxidized to harmful NO_x when the syngas is combusted. Much is known about nitrogenous impurities from gasification of coal since this field has been studied widely [16]. However, experience showed that those results can’t be applied on gasification of biomass since nitrogen is bound in different forms in coal and biomass [16]. The fuel structure, which has a major influence on the behavior fuel-bound nitrogen differs for coal and biomass. Hence, a lot of research is necessary on this field. Additionally, it is necessary to find methods to purify the syngas afterwards, which is often challenging due to the great variety of impurities [17]. Methods such as hot and cold gas cleaning, scrubbing, gas filtration and catalytic gas cleaning are the most promising and hence topics of research [21].

2.3 Formation of nitrogenous emissions during combustion

The formation of nitrogenous emissions during the combustion is a complex process. In general, NO_x and N_2 are the final products. Depending on the fuel, mainly from coal, N_2O can also be formed in significant amounts. The formation of nitrogen compounds is influenced by various factors such as chemical composition of the fuel, but also the combustion process itself and the surrounding atmosphere has an influence [14]. Also, different types of nitrogen sources must be considered. Generally, three types of paths for NO_x formation are distinguished: thermal NO_x, prompt-NO_x and fuel-NO_x [14]. Thermal NO_x and prompt-NO_x are formed by the reaction of elemental nitrogen in the atmosphere with oxygen or the fuel. Those reactions can be neglected in fluidized bed systems due to the relatively low temperatures. Hence, the focus in this thesis is only on fuel-NO_x.

Fuel-NO_x is formed by various mechanisms which vary between the stages of the combustion. Around 75% of NO_x is formed during pyrolysis and around 25% during char oxidation [14]. The formation mechanisms during pyrolysis and char combustion are described in the following.

Pyrolysis

During pyrolysis, volatile compounds are released to the gas phase. Non-volatile compounds remain in the solid residue, which is called char [22]. To understand the distribution between volatile nitrogen and char-nitrogen, it is essential to have knowledge about the chemical composition of the fuel. In biomass, proteins are a major source of nitrogen [23]. The proteins contain various amino acids which include amino groups of the form $-NH_2$. From those amino groups NH_3 can be released easily to the gas phase. NH_3 can then react with oxygen in the gas phase resulting in the formation of NO_x. NH_3 can also react with NO that has already been formed in a comproportionation reaction to elemental nitrogen [14].

$$2\,NH_3 + 2\,O_2 \rightarrow 2\,NO + 2\,H_2O + H_2 \qquad (8)$$

$$2\,NH_3 + 2\,NO \rightarrow 2\,N_2 + 2\,H_2O + H_2 \qquad (9)$$

The above described mechanism explains why N_2O formation is low for biomass combustion. NH_3, an important pre-cursor for NO_x formation, is unlikely to form N_2O. However, NH_3 is not the only nitrogen containing product which is released during pyrolysis. Nitrogen can also be released as HCN, HCNO or in tar. HCN can also be oxidized to NOx when reacting with oxygen. In addition, HCN can react to N_2O. It is believed that HCN is mainly formed by cracking of larger fragments which are released to the gas phase [23, 24]. Several studies suggested that NH_3 and HCN are formed by competing mechanisms [23]. At lower temperatures NH_3 is believed to be the main species. When the temperature is increased to above 900 °C, HCN can become the dominant species. At a given temperature the NH_3/HCN ratio can also be influenced by the particle size. Smaller particles are more likely to release HCN since the particles have a higher temperature in their interior [23]. In addition, ash-forming elements are believed to have an influence on the NH_3/HCN ratio. Earlier studies demonstrated for some biomasses how a higher amount of Ca and K can increase the NH_3 formation during pyrolysis [24].

Char combustion

Char combustion is a complex process and the reactions that occur are influenced by various factors. Unlike to the pyrolysis, the NO_x-formation during char oxidation is a reaction between the gas phase and solid phase. Char-nitrogen is oxidized by oxidizing agents from the surrounding atmosphere without prior formation of pre-cursors. The reactivity of chars and the char-nitrogen towards oxidation varies depending on the fuel, combustion conditions and the conditions how the char was produced [25]. For instance, biomass forms less char than coal. However, biomass chars show a higher reactivity than coal chars [25, 26]. The reactivity of the char is also higher when the char is produced at lower temperatures.

Interestingly, the formation rate of NO_x increases during char combustion. This is a result of the decreasing particle size and an indicator that the reaction takes place inside the fuel particle [26]. The formed NO_x can be reduced inside the fuel particle to N_2 by the char itself [14, 27]. Also, NO_x can be reduced by CO from the gas phase with the char acting as a catalyst [25]. Especially at higher temperature the catalytic reaction between CO and NO is relevant. The reduction of NO in the char is possible because of the catalytic active sites in the char. The gases diffuse through the particle and reactions can take place when the molecules reach active sites [27]. During char oxidation, the particle size decreases. This means less surface and less active sites where NO can be reduced. As a result, one can observe the increasing NO_x formation which has already been mentioned. Ash forming elements are important components of those active sites. CaO, MgO and Fe_2O_3 have an important influence on the reduction of NO_x during char combustion [14]. Recent studies revealed that the NO_x formation is higher for biomass in which those catalytic active sides are missing [28]. Demineralized biomass showed up to 70% conversion from char-nitrogen to NO_x while the original biomass had only 15-30% conversion [28].

Knowledge about such mechanisms, in which NO_x and other nitrogenous emission are formed during pyrolysis and char combustion, is essential to be able to control and reduce emissions in combustion processes. Hence, the main objective of this work was to investigate, how various pre-treatment methods for biomasses influence the formation of NO_x. The formation of ammonia was also studied to get a better understanding about pre-cursor formation and factors which can affect it. Furthermore, the influence of different gaseous environments on the combustion of those biomasses is investigated to get a better understanding of the NO_x formation from the char.

2.4 Kraft-Recovery Boiler

An important source for bio-energy is black liquor. Black liquor is a waste product from pulping industry [29]. Especially in Finland black liquor is covering a huge amount of power production from biomass. Around 46% of the total bio-energy in Finland is produced by black liquor combustion which corresponds to 11% of the total heat power [30]. In 2013, the worldwide production of black liquor from pulping industry was more than 130 million tonnes [31]. Black liquor is a mixture of organic material, water and the inorganic chemicals that are used for the pulping process. The inorganics are mainly Na_2S and NaOH which are converted to Na_2SO_4 during the pulping process. Around 2/3 of the solid material is organic material, mostly lignin, and around 1/3 is inorganics [29].

To extract energy from black liquor, a special type of boiler, the so-called Kraft-Recovery Boiler, is used [30]. Fig. 4 shows a simplified sketch of such a recovery boiler. The purpose with the Kraft recovery boiler is not only to extract the energy from the black liquor, but also to reconvert the inorganic chemicals so that they can be re-used in the pulping process. Therefore, several stages in the boiler are needed. Firstly, the black liquor is pumped into the boiler and spread as small droplets using a special nozzle [30]. More than 80% of the organic material is volatile which means that a large part of the organics is already combusted in the oxidizing atmosphere before the char and the inorganics reach the char bed. The obtained heat from the combustion of those organics is exchanged at heat exchangers and used to produce power for the pulping process.

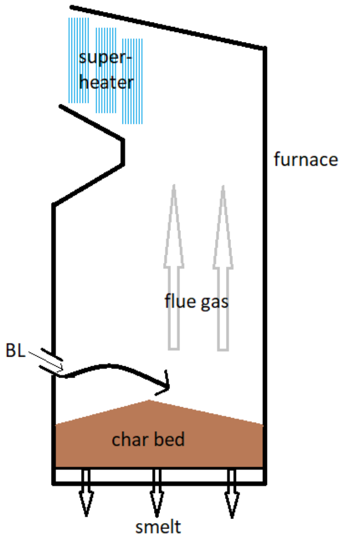

Fig.4 Kraft Recovery Boiler.

In the char bed a reducing zone prevails, and only little oxygen is available. The purpose is to reduce Na_2SO_4 to Na_2S which can then be re-used in the pulping process. Sulfate is here an oxidizing agent in reactions with char carbon since oxygen is not available. The char-carbon is oxidized to CO and CO_2 and sulfate reduced to sulfide.

As in combustion of other biomasses, control of NO_x emissions is also a challenge in Kraft-recovery boilers. The formation of NO_x from black liquor has not been studied as extensively as for other fuels since nitrogen contents in black liquors are rather low. However, NO_x emissions from black liquor cannot be neglected. Hence, a smaller part of this thesis is also focusing on the NO_x formation from black liquors. The objective was also to test, if the new set-up for the determination of ammonia formation from pre-treated biomasses can be applied on experiments with black liquor.

3. Experimental

3.1 Biomass and pre-treatments

In this thesis. spruce bark and wheat straw have been used to investigate the influence of various pre-treatment methods on those biomasses. The spruce bark samples were pre-treated with steam-explosion, torrefaction and washing followed by torrefaction. Torrefaction and washing+torrefaction were also applied on wheat straw. The samples were not pre-treated in house but already received in the pre-treated form.

For the washing pre-treatment, the biomass was put in a tank with fresh tap water which was then heated up to 50 °C. After 1 hour, the biomass was taken out from the tank and sprayed with fresh tap water. Afterwards it was dried until the moisture content was below 15 wt%. The torrefied samples were first dried at a temperature between 150 and 180 °C. In the next step the spruce bark was torrefied at 230 °C and the straw at 250 °C. The resulting mass yields for the samples were 65% and 69% respectively.

For further usability in the laboratory, an ordinary household mixer was used to pulverize the provided samples. Only the original wheat straw was not brittle enough to be pulverized. Still, the straw could be chopped into small pieces which could be used for the experiments. Fig. 5 shows the pulverized sample. The chemical compositions of the samples have been analyzed with CHNS-analysis for the organic compounds and ICP-OES for the inorganic compounds, i.e. the ash-forming elements. The analyses were performed in an external laboratory as well.

The combustion experiments were performed in the so-called single particle reactor (SPR) which will be described in the following chapter. The biomass samples were pressed to pellets so that they could be used in the experiments with the SPR. The pellets had a diameter of 8 mm, height of around 3 mm (slightly varying depending on the biomass) with a mass of 100 mg. To measure moisture contents, some pellets of each sample were dried in an oven for 24 hours at 100 °C. The mass differences were used to determine the moisture contents.

Fig. 5 Biomass samples after different pre-treatments; spruce bark (A), steam-exploded bark (B), torrefied bark (C), washed and torrefied bark (D), wheat straw (E), torrefied straw (F), washed and torrefied straw.

3.2 Single particle reactor

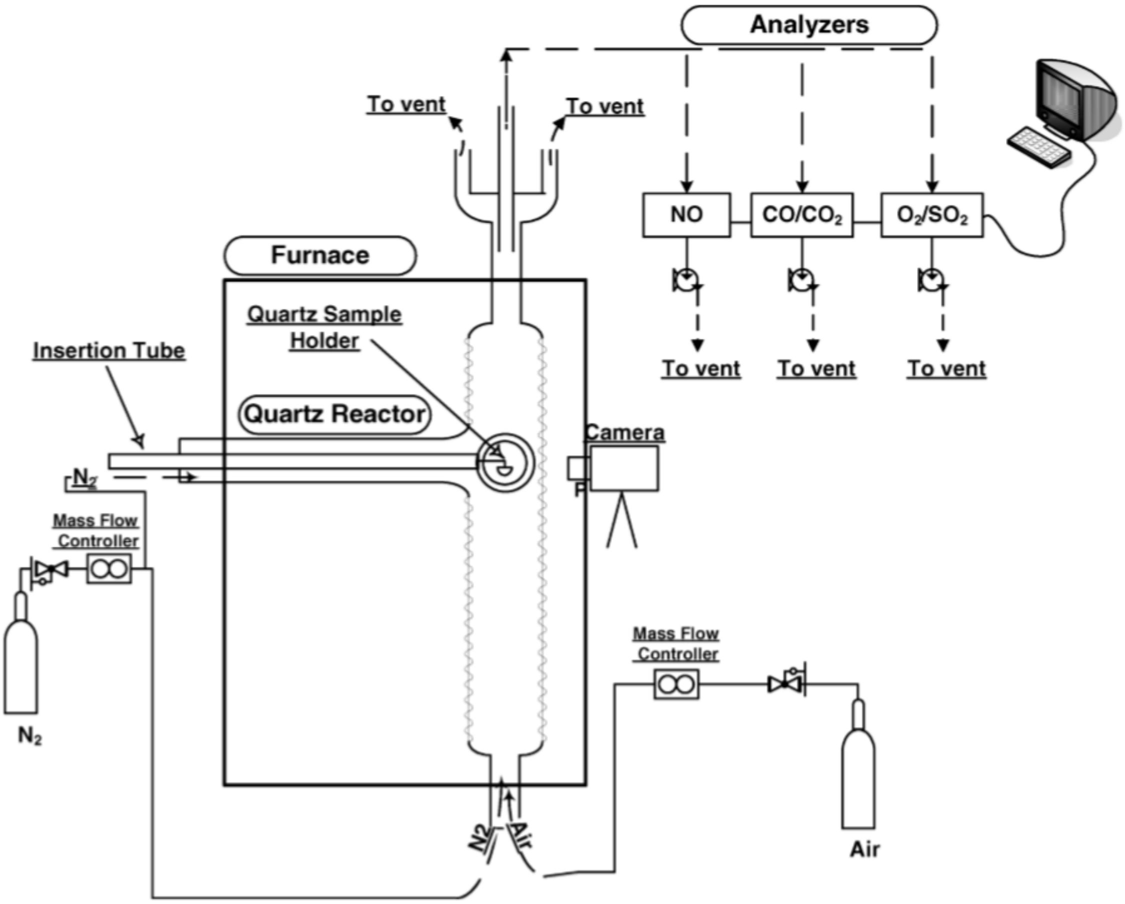

Fig.6 Single particle reactor [33].

Fig. 6 presents the single particle reactor which was used for the combustion experiments. The core of the SPR is a quartz reactor in which the combustion takes place. The quartz reactor is inserted in a furnace which can be heated up by an electrical heater and the temperature can be controlled with a thermocouple inside the furnace. The samples are put into the reactor on a quartz sample holder via an insertion tube which is flushed with pure N_2. The sample is kept in this insertion tube until the conditions in the reactor are constant. The sample is then moved to the center of the quartz reactor where the combustion takes place. The combustion air is coming from underneath and depending on the desired gas mixture, pure N_2 is added from the bottom and the side of the reactor. The flow coming from underneath was for all experiments 100 l/h at NTP and the total flow coming out of the reactor was 220 l/h at NTP.

After leaving the reactor, the flue gas is directed to a setup with continuous analyzers for NO, CO, CO_2. NO concentrations are measured by a chemiluminescence analyzer, CO and CO_2 by a non-dispersive infrared analyzer and for O_2 a combined paramagnetic and infrared analyzer is used. Using the equation for an ideal gas, the measured concentrations can be converted to the mass flow of the elements

$$\dot{m} = \dot{n} \cdot M = \frac{p \cdot \dot{V}}{R \cdot T} \cdot M \qquad (10)$$

The mass flow $\dot{m}$ is the product of the amount of substance $\dot{n}$ in $\frac{mol}{s}$ and the molar mass. The amount of substance can be calculated using the pressure p of the gas, volume flow $\dot{V}$, ideal gas constant R and the temperature T (here 303 K). The integration of $\dot{m}$ gives the total mass of the elements in the measured gases, e.g. how much N is found in NO or how much C is found in CO and CO_2. Knowing the chemical composition of the biomass, those results can then be used to calculate conversions for those elements in the biomass.

3.3 Quantification of NH_3

With the setup presented in 3.2, the only form of nitrogen that can be measured is NO. Since the setup did not include a device to measure other forms of nitrogen online, a new device was added to quantify NH_3 by using wet chemistry methods. Fig. 7 shows the additional setup. The gas coming from the reactor is directed to a glass bottle which is filled with 50 ml of a 1 M aqueous solution of hydrochloric acid. The bottle was cooled down using an ice bath to prevent evaporation of the aqueous solution due to the hot flue gas. The aqueous solution of HCl was used to convert all incoming NH_3 to NH_4^+ ions. The NH_4^+ ions are dissolved in the solution and can later be quantified. Before the analysis, the solution has to be filtered because ash particles can also be blown into the bottle which would interfere during the analysis of NH_4^+ concentrations. Tests with the obtained solution in a micro gas chamber confirmed that the formed NH_3 can be collected in the bottle. Quantitative analysis of NH_4^+ were done using two different methods.

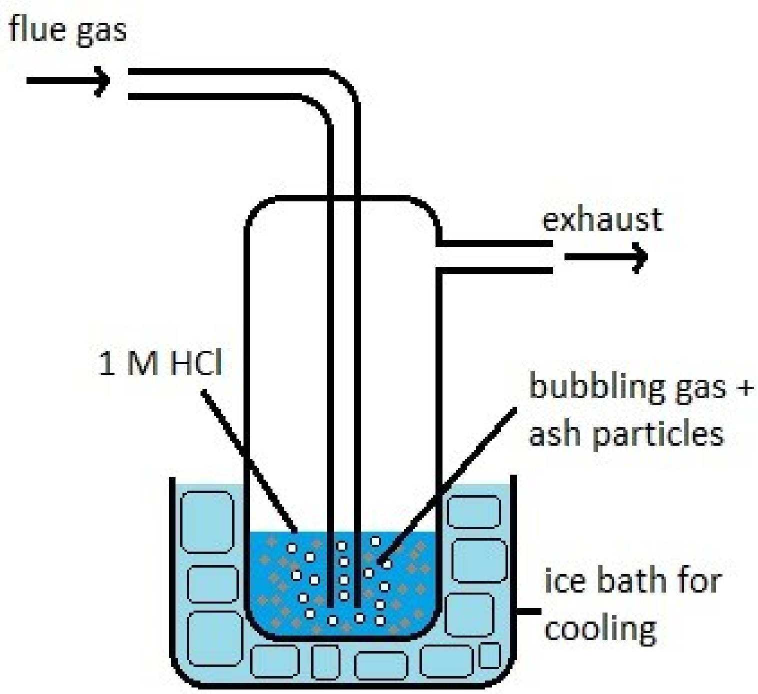

Fig. 7 Device to capture released NH_3 from the flue gas.

Two different methods have been used in order to verify that the results are not affected by different types of analysis methods. Also, samples with known concentrations have been analyzed to check if the method is suitable. The first analyses have been performed by Labtium, Finland, using the Kjeldahl method. The second analyses were performed by ALS Scandinavia using spectrophotometry. From the obtained concentrations the total amount of formed NH_3 could be obtained and thus, also the conversion of the fuel nitrogen to ammonia.

The experiments in which ammonia was collected were all performed in 100% N_2 atmosphere. The first tests were carried out with around 2 g of samples per biomass. 10 pellets à 200 mg were devolatilized one by one in the reactor. The reactor was always flushed with N_2 to ensure that only pyrolysis gases are analyzed and that no further oxidation of those pyrolysis gases can occur. For the second tests a total mass of 6 g per biomass was used. The higher amount was chosen to minimize mistakes that can occur due to smaller amounts of ammonia that might stick on the pipe from the reactor to the bottle with the acid solution. Samples with known concentrations were analyzed in order to test the two analysis methods. Both methods showed good accuracy for concentrations below 150 mg/l. The highest concentration of the actual samples was 128 mg/l. Therefore, all measured concentration should be accurate or both the test row with 2 g and 6 g of sample per biomass.

3.4 Black liquor

The experiments with the black liquor were also performed in the SPR described in chapter 3.2. For the experiments, a black liquor droplet of the mass of around 50 mg is attached to a grid that can be inserted into the reactor. The droplet sticks to the grid due to the high viscosity of the black liquor. The combustion experiments were performed in various atmospheres containing different mixtures of O_2, CO_2 and steam at 900 °C.

For the investigation of the NH_3 formation from pyrolysis of the black liquor, droplets of the black liquor were put into the reactor in pure N_2-atmosphere at 900 °C. A total amount of 6 g of sample was used. NH_3 was analyzed using the method described in chapter 3.3.

4. Results and discussion

4.1 Composition of treated biomasses

All analysis results presented in this chapter are from own laboratories. The values obtained from the extern laboratory can be found in the appendix. Tab. 2 lists the contents of carbon, nitrogen, hydrogen and sulfur for the bark samples. Furthermore, the char yield after 2 min in pure nitrogen at 850 °C is given and also ash yields after complete combustion in 10% oxygen-containing atmosphere at 850 °C. Original bark has the lowest carbon content of all bark samples. Steam-exploded bark has a similar carbon content. Torrefaction and washing + torrefaction pre-treatments increase the carbon content slightly. Washed + torrefied bark has with 56.1% the highest carbon content of the investigated samples. With an increasing carbon content, the char char-yield is also increasing for those samples. Nitrogen contents are for all pre-treated samples slightly lower compared to the original bark. Still, a notable trend for the nitrogen contents cannot be observed. Steam-exploded bark has the lowest nitrogen content, which is around 20% lower than in the untreated sample. Washed + torrefied bark has the second lowest nitrogen content.

Tab. 2 Elemental analysis of bark after different pre-treatments

wt% ds	**C**	**N**	**H**	**S**	**char (850 °C)**	**ash**
original	49.3	0.48	5.78	0.022	20.6	1.5
steam-exploded	50.5	0.39	5.88	-	23.6	1.9
torrefied	54.1	0.45	5.07	-	31.9	1.8
washed + torrefied	56.1	0.41	5.09	-	31.7	1.8

However, as described in the introduction, the amount of NO emissions is not only dependent on fuel-nitrogen contents, but it is also influenced by many other factors. Earlier studies showed that the amount and composition of the ash-forming matter influences the nitrogen chemistry, both during pyrolysis and during char combustion. Fig. 8 shows the contents of the ash-forming elements with the highest contents in original spruce bark. Calcium is here the most abundant ash-forming element. Other alkali metals and alkaline earth metals such as potassium, magnesium, barium, sodium and strontium can be found in smaller concentrations. The value for silicon stated in Fig. 8 is an average value taken from literature due to difficulties during silicon analyses of the bark samples [32].

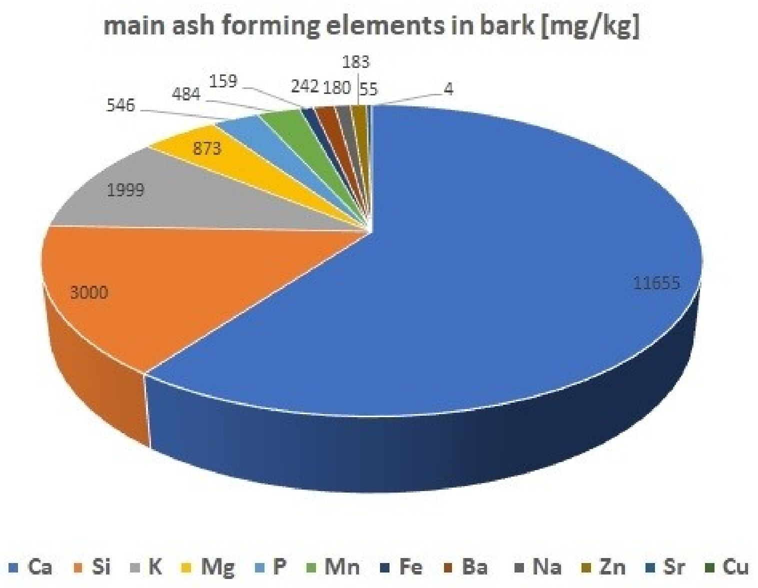

Fig. 8 Main ash-forming elements in original spruce bark [mg/kg dry biomass].

Tab.3 Amounts of ash-forming elements after pre-treatments

[mg/kg dry bark]	Ca	K	Mg	Ba	Na	Zn	Sr
original	11656	1999	873	241	180	184	55
steam-exploded	10124	1978	719	213	144	131	41
torrefied	15959	2355	1081	324	226	219	67
washed + torrefied	14482	1899	919	254	209	202	62

Table 3 shows the concentrations of some major ash-forming elements in all spruce bark samples. For all elements one can observe similar trends for their concentrations after the pre-treatments. In torrefied bark the contents are always the highest. This can be explained by the torrefaction process. The mass of the fuel is reduced while the amount of ash-forming matter is believed to stay the same. This leads to an enrichment of those ash-forming elements. Washing before the torrefaction can diminish this effect because parts of the inorganics in the biomass can be dissolved. Especially potassium concentrations can be decreased. The same trends can be found also in the analyses from the commercial laboratory. Only for the steam-exploded bark, the results differ. Increasing concentrations of all ash-forming elements can be observed while own results show decreasing concentrations in steam-exploded bark compared to the original biomass.

For straw, the pre-treatments have almost the same effect on chemical composition as for bark. Tab. 4 shows the ultimate analysis results for the pre-treated straw samples. Carbon contents are higher after the pre-treatments while hydrogen and sulfur contents are lower. Also, the char yield is higher as well as the amount of ash. The nitrogen content is higher after torrefaction but is lower after the washing process. As in bark, no trend depending on the pre-treatments can be observed for the fuel nitrogen content.

Tab. 4 Ultimate analysis of wheat straw after different pre-treatments

wt% ds	C	N	H	S	char (850 °C)	ash
original	42.7	0.57	5.45	0.055	15.1	7
torrefied	44.9	0.65	5.31	0.044	21.8	8.7
washed + torrefied	47.3	0.45	5.38	0.032	23.8	8.1

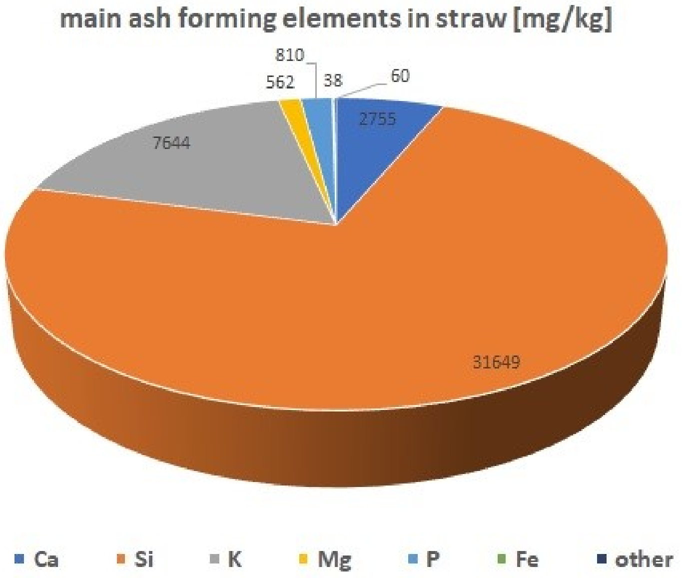

Fig. 9 Main ash-forming elements in original wheat straw [mg/kg dry biomass].

Fig. 9 shows the concentrations of the major ash-forming elements in the original straw. One can see, that the composition of the ash-forming matter is different compared to bark. Silicon represents the biggest part of inorganic elements. Calcium occurs in straw in much smaller concentrations - around one fourth of the concentration in bark. Potassium, on the other hand, can be found in four times higher concentrations compared to bark. In general, the variation of ash-forming elements is not as high in straw as in bark. In bark, 10 elements could be found with concentrations higher than 100 mg/kg. In straw it is only five elements.

Tab. 5 lists the concentrations of the four ash-forming elements which occur in wheat straw in high concentrations. Here the same observations can be made as for the bark samples. The torrefied sample usually has the highest concentrations. Only the potassium concentration is lower for torrefied straw compared to the original straw. However, in the commercial laboratory analysis also torrefied straw has the highest concentration of potassium. In general, the ÅA-results results differ more from the commercial analysis results for straw as compared to bark. This might be due to the higher inhomogeneity of the straw samples as compared to the bark samples. However, similar trends can be observed in both cases. Interestingly, around half of the potassium in straw is removed by the washing treatment. This is not the case for bark.

Tab.5 Amount ash-forming elements after pre-treatments

[mg/kg straw]	Ca	Si	K	Mg
original	2756	31650	7644	562
torrefied	3430	36965	7102	859
washed + torrefied	3614	29698	3238	531

4.2 Evaluation of the experimental method (SPR)

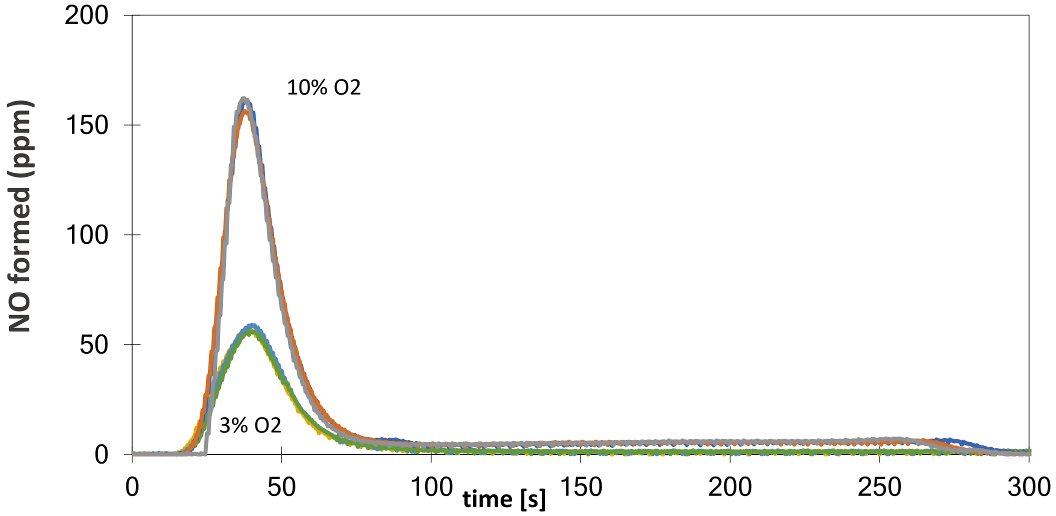

Fig. 10 NO-formation from combustion of steam-exploded bark in SPR in 3% O_2 and 10% O_2.

Fig. 10 exemplifies NO concentration curves from the combustion of steam-exploded bark samples in an atmosphere containing 3% and 10% oxygen at 850 °C. Here, 0 s is the starting point at which the particle is inserted into the reactor. The residence time distribution of the reactor system is not considered here so curves actually lack a bit behind in time. However, since only the integral is important for the evaluation, the difference can be neglected. It can be seen that the curves only vary little for several repetitions of the same experiment. This confirms that measurements in the single particle are reproducible. Hence, three repetitions per sample were considered to be sufficient to obtain representative results. The curves were not only reproducible for NO but also for other emissions such as CO_2.

Tab. 6 Check of accuracy for single particle reactor

		C in fuel [wt%]	C as CO_2 [wt%]	yield
bark	original	46.9	43.8	94%
	steam-exploded	46.0	44.3	96%
	torrefied	52.1	50.9	98%
	washed + torrefied	53.9	50.5	94%
straw	original	38.2	37.9	99%
	torrefied	43.1	40.8	95%
	washed + torrefied	45.5	42.8	94%

CO_2 was used to calculate a mass balance to check if there are possible mass losses during the experiments. Samples were combusted in an atmosphere with 10% oxygen and it can be expected that almost all carbon is oxidized to CO_2. Tab. 6 shows that most of the carbon from the fuel can be found in the CO_2. Since elemental analyses and experiments in the SPR give similar values and almost closed mass balance, it can be assumed that both the elemental analyses and the single particle reactor have a high accuracy.

4.3 Stages of combustion

In the combustion tests, the different combustion stages can be observed. During the first ~60 s a rapid increase of concentrations followed by a rapid decrease of concentrations can be observed. During this stage, i.e. pyrolysis, the volatiles are released. The next stage is char combustion. Here one can observe lower concentrations during a significantly longer time. In fig. 11 the different stages are marked based on the NO-concentration curve. The curves for pyrolysis and char combustion are extended with lines and their intersection is here defined as the transition from pyrolysis to char combustion.

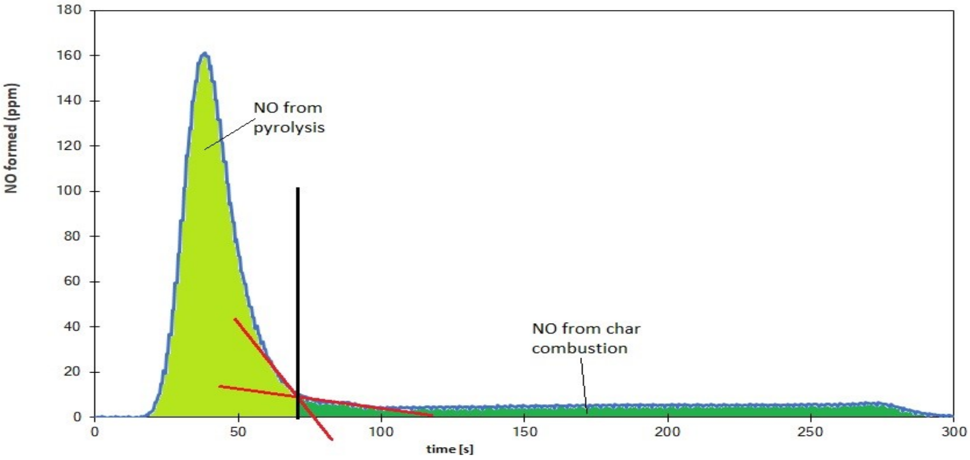

Fig. 11 Integration of NO concentrations from pyrolysis and char combustion.

The various stages are documented in fig. 12 and 13. The pictures in fig. 12 are taken during the combustion of a bark sample and in fig. 13 during the combustion of a straw sample in 10% oxygen. In the first step (1), the particle is drying. After a few seconds pyrolysis starts (2 + 3). Flames were only visible during pyrolysis in the atmosphere with 10% oxygen, not with 3% oxygen. The pyrolysis of the used bark and straw samples last for around 60 seconds followed by char oxidation (4). During char oxidation the particle is glowing, and no flame is formed.

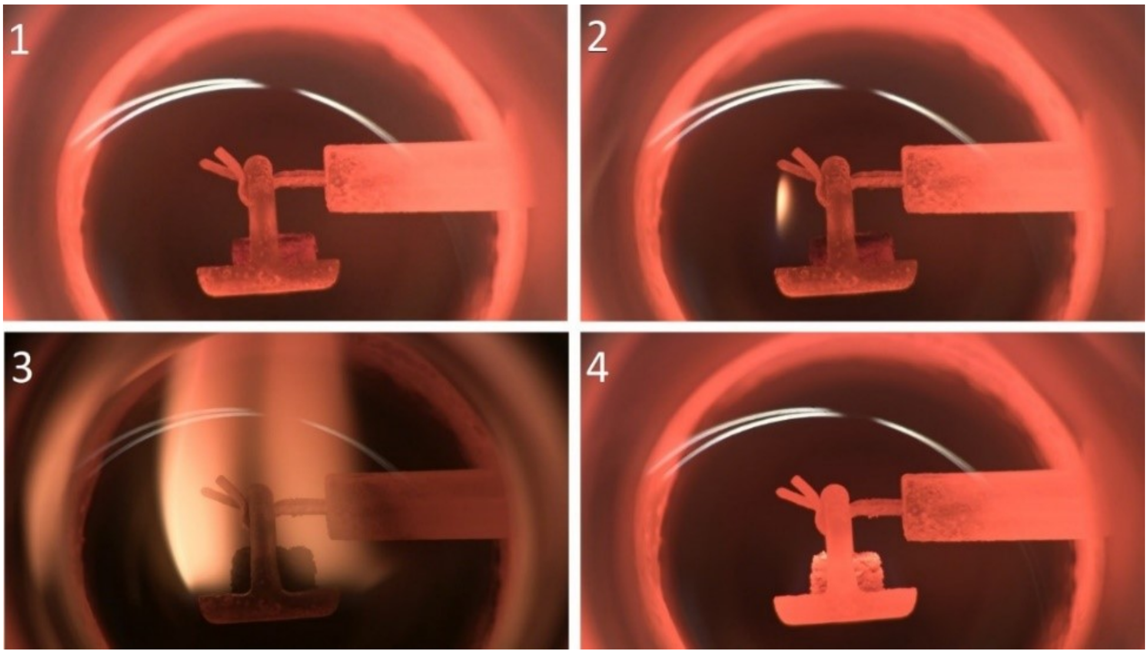

Fig. 12 Combustion stages of bark in SPR in 10% O_2/N_2; 1 – drying, 2/3 – pyrolysis, 4 – char combustion.

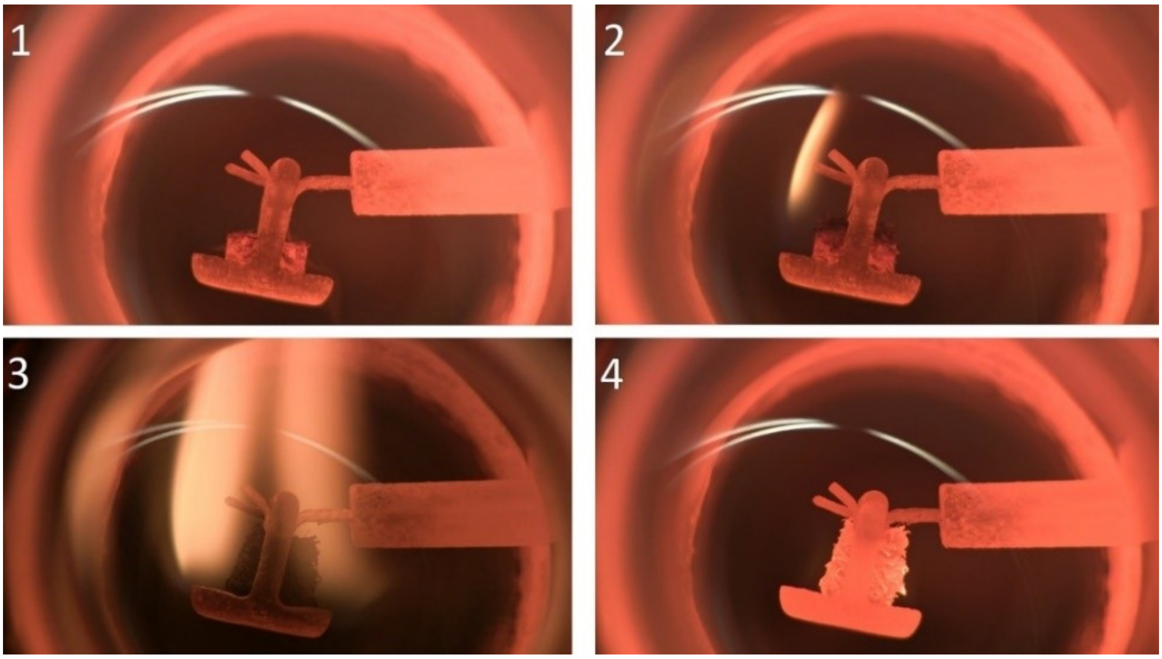

Fig. 13 Combustion stages of straw in SPR in 10% O_2/N_2; 1 – drying, 2/3 – pyrolysis, 4 – char combustion.

4.4 NO emissions from biomass combustion

Fig. 14 shows the NO-emissions and the conversions of the fuel nitrogen to NO from the biomasses in 3% and 10% oxygen. For all fuels the NO emissions are much higher in 10 % oxygen compared to 3% oxygen. Nevertheless, one can observe the same trends for the various pre-treated samples under both conditions. Hence, most results will here only be discussed based on the data obtained from the experiments with 10% oxygen.

For both straw and bark, the torrefied samples show the highest NO-emissions. The washed and torrefied samples have lower emissions as compared to the torrefied samples. They are slightly higher, however, than emissions from the untreated samples. Only the steam-exploded bark had lower emissions than its untreated equivalent. NO emissions are here around 20% lower, which is a significant reduction. Comparing those results with fuel-nitrogen concentrations (see tab. 2 and 4), one can notice that the NO-emissions do not follow the same trend. For bark, all pre-treated samples had lower nitrogen concentrations than the original bark. However, only steam-exploded bark has also lower NO-emissions while the other two show increased emissions.

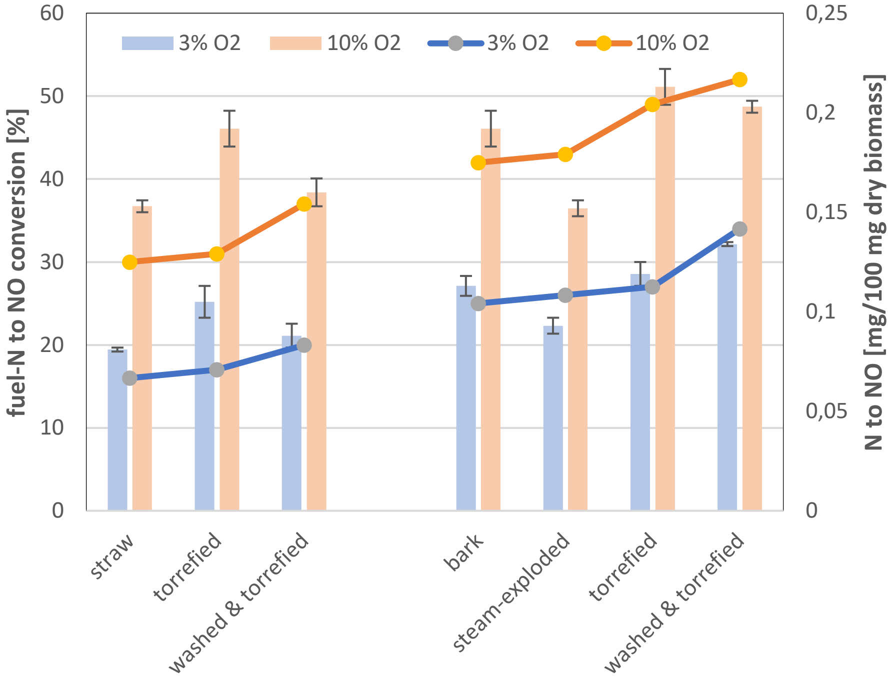

Fig. 14 NO emissions for combustion of biomasses in 3% and 10% O_2/N_2 (bars) at 850 °C and conversion of fuel-N to NO (dots).

The same can be observed for the straw samples. Washed + torrefied straw has slightly higher NO- emissions although the fuel contains around 20% less nitrogen. Looking at the conversions instead of the total emissions shows that all pre-treated samples have a higher conversion of fuel nitrogen to NO than the untreated samples. For both biomasses the washed + torrefied samples were found to have the highest conversions.

To understand the obtained results, it is necessary to get a better picture regarding how NO is formed during combustion and how the NO formation steps are influenced by the pre-treatment methods. As already described in chapter 4.3, combustion takes place in different steps whereas pyrolysis and char combustion are the most relevant steps. During pyrolysis, volatile nitrogen is released in form of pre-cursers which can then be oxidized to NO, for instance, if an oxidizing agent is present in the atmosphere. The char nitrogen on the contrary remains in the char.

Fig. 15 shows the share and total amount of volatile and char nitrogen in the investigated samples. All pre-treated samples show an increased share of char nitrogen. The torrefied and washed + torrefied samples have the highest share of char nitrogen. The amount of volatile nitrogen is reduced in the pre-treated samples in general. Torrefied bark is the only exception.

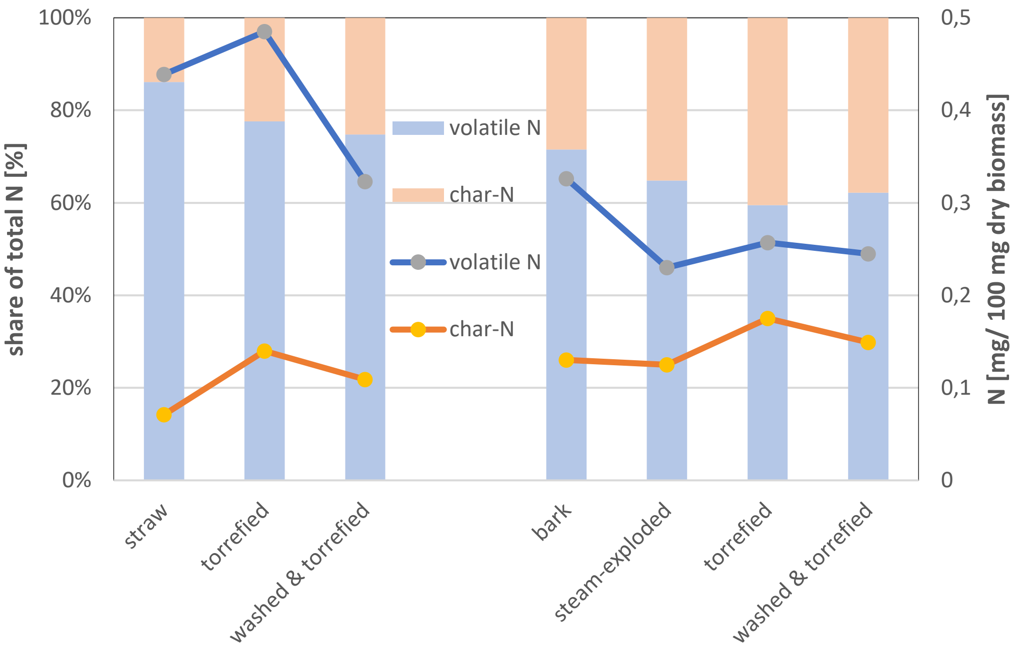

Fig. 15 Amounts of volatile nitrogen and char-nitrogen in biomass based on ultimate analysis of original biomass, char (90 s in N_2, 850 °C) and ash.

Fig. 16 shows the NO-emissions for char oxidation and pyrolysis separately. Significantly more NO is formed from pyrolysis than from char combustion which is typical for biomasses. Comparing the emissions from the char combustion with the amount of char nitrogen shows a similar trend. Steam-exploded bark has a lower char nitrogen content and emits less NO during char oxidation. Torrefied and washed + torrefied biomasses contain a higher amount of char nitrogen and have higher char-NO-emissions. The same observations can be made for straw. Here it can also be mentioned that the total amount of released NO is basically the same for the combustion in the atmosphere with 10% and 3% oxygen. The only difference here is that char combustion is much faster when more oxygen is present.

The NO emissions from the char combustion can be influenced by many factors. Other studies report, for instance, that there is a correlation between ash-forming matter contents and NO emissions [25, 28]. Calcium may be one of the ash-forming elements that contributes to this effect. Karlström et al. showed for some biomasses, that NO emissions are lowest at high calcium concentrations because of reduction of NO due to catalytic activity. In this thesis, the trend could not be observed. The only factor which has here an observable factor on the NO emissions from char oxidation is the amount of char nitrogen.

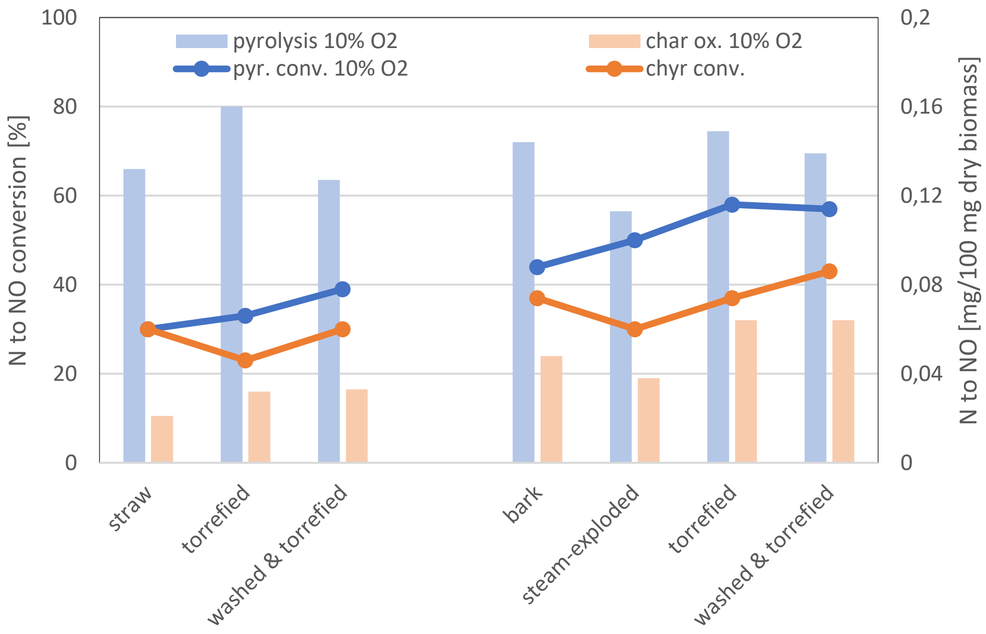

Fig. 16 NO emissions for pyrolysis and char combustion of biomasses in 10% O_2/N_2 at 850 °C.

If the same correlation between char-nitrogen content and NO-emissions would also be valid for NO formation during pyrolysis, one could expect lower NO emissions from pyrolysis for pre-treated biomasses due to their lower content of volatile nitrogen. Fig. 16 shows that this is clearly not the case. Most pre-treated samples show similar or even higher NO formation. Only steam-exploded bark has lower emissions compared to the original bark. Still, even for this sample the conversion is higher than for the untreated sample. An increase of the conversion can be observed for all pre-treated samples. While 44% of the volatile nitrogen in the original bark is converted to NO during pyrolysis, this value is increased to 58% for torrefied bark and 57% for washed + torrefied bark respectively. For straw the value is increased from 30% in original straw to up to 39% in the washed + torrefied straw.

Since significantly more NO is emitted during pyrolysis compared to char oxidation, it is worthwhile to have a closer look on the pyrolysis. As already described in the introduction, pre-cursors play an important role in NO formation during pyrolysis. The amount of pyrolysis-NO is not proportional to the amount of volatile nitrogen, implying that there are other factors than only the amount of volatile nitrogen which cause changes in pre-cursor formation. For this reason, the investigation of NH_3 formation during pyrolysis was of interest. The results are presented in the following chapter.

4.5 NH_3 formation tendency during pyrolysis

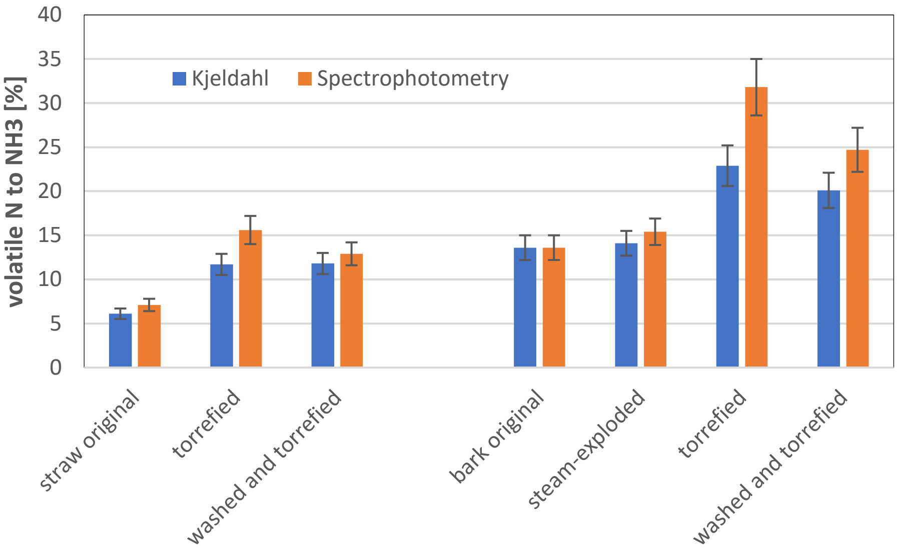

Fig. 17 volatile N to NH_3 formation during pyrolysis in N_2 at 850 °C.

Fig. 17 shows the obtained data for the conversion of volatile nitrogen to NH_3. First of all, one can observe that the values are higher for the second test row in which spectrophotometry has been used for analysis. As mentioned earlier, in the second tests 6 g of sample were used per biomass compared to only 2 g in the first tests. One explanation could be the compensation of possible losses when higher amounts are used. Small losses have a smaller impact when the total mass is higher, but a larger impact when less biomass is used. Still, the results from both test rows show similar. The data from the second tests using spectrophotomtery are used in the following discussion, since those values might be closer to the real values.

Generally, the conversion of volatile nitrogen to NH_3 is lower in straw than in bark. In untreated straw, 7% of the volatile nitrogen is converted to NH_3 while it is around 14% in bark. The value for steam-exploded bark is only slightly higher than for the untreated bark. For both straw and bark, torrefaction and washing + torrefaction increased the value whereas torrefied samples have the highest conversion. With 16%, the conversion in torrefied straw is more than twice as high as in untreated straw and also washed + torrefied straw has a much higher conversion with 13%. The same can be observed for bark. The conversion in torrefied bark (32%) is also more than twice as high compared to untreated bark. In washed + torrefied bark around 25% of the volatile nitrogen is converted to NH_3.

The drastic changes for the observed NH_3 might be explained by the ash forming elements. As mentioned in the introduction, earlier studies showed that calcium and potassium may influence the ammonia formation for some biomasses. Fig. 18 shows the correlation between calcium concentrations in the samples and conversions of volatile fuel-nitrogen to ammonia. Straw has a relatively low calcium content compared to bark. The concentration of calcium in untreated bark is around 3600 mg/kg and the conversion around 7%. In torrefied straw the calcium concentration is increased to almost 4200 mg/kg and also the conversion to ammonia is increasing. Washed and torrefied straw has slightly less calcium than torrefied straw and at the same time a slightly lower conversion to NH_3. The same correlations can be observed for the various bark samples. Untreated bark has 8880 mg/kg calcium and 14% conversion which are the lowest values for all bark samples. Torrefied bark has 14200 mg/kg calcium and 32% conversion which are the highest values of all bark samples.

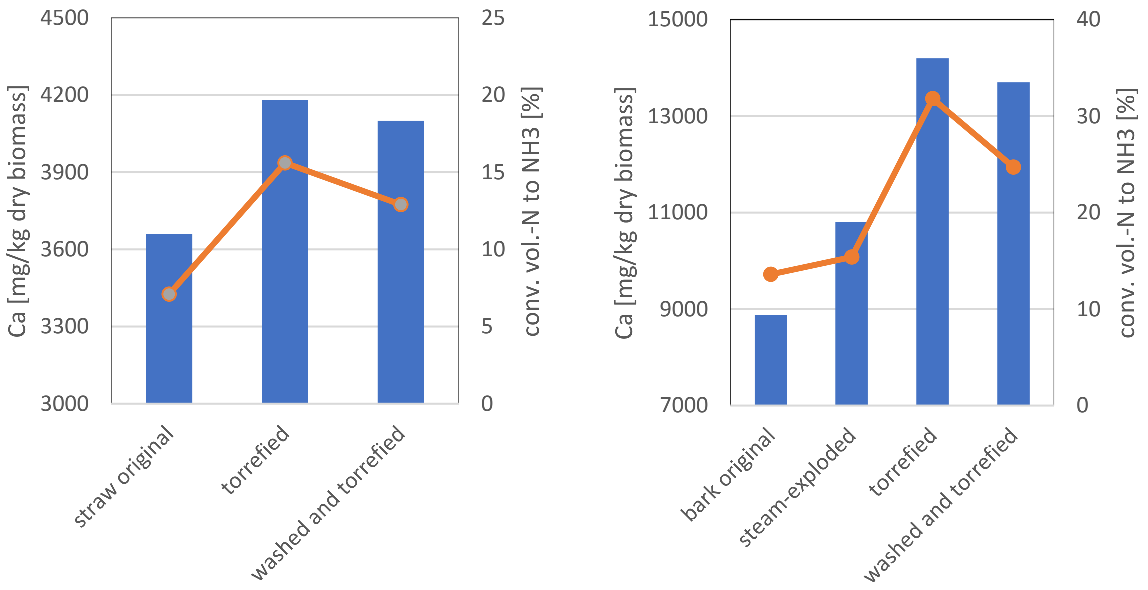

Fig. 18 Correlation between fuel-N to NH_3 conversion and amount of Ca in biomass.

Based on those findings one can say that there may be a correlation, i.e. catalytic activity, between calcium concentrations in the biomass and the conversion of volatile nitrogen to NH_3. On the other hand, no indications could be found for the catalytic activity of potassium which is described in other publications [24]. Fig. 19 shows the conversions of volatile nitrogen to ammonia versus potassium concentrations.

The potassium concentration is much higher in straw as it is in bark. In the untreated bark the potassium content was 7500 mg/kg. The torrefied straw sample has almost the same potassium content, but the conversion is twice as high. The washed + torrefied sample contains much less potassium compared to the untreated sample, but the conversion to NH_3 is still much higher than in the untreated sample. For bark one can also observe that there is obviously no clear connection between potassium concentrations in the biomass and the conversion of volatile nitrogen to NH_3.

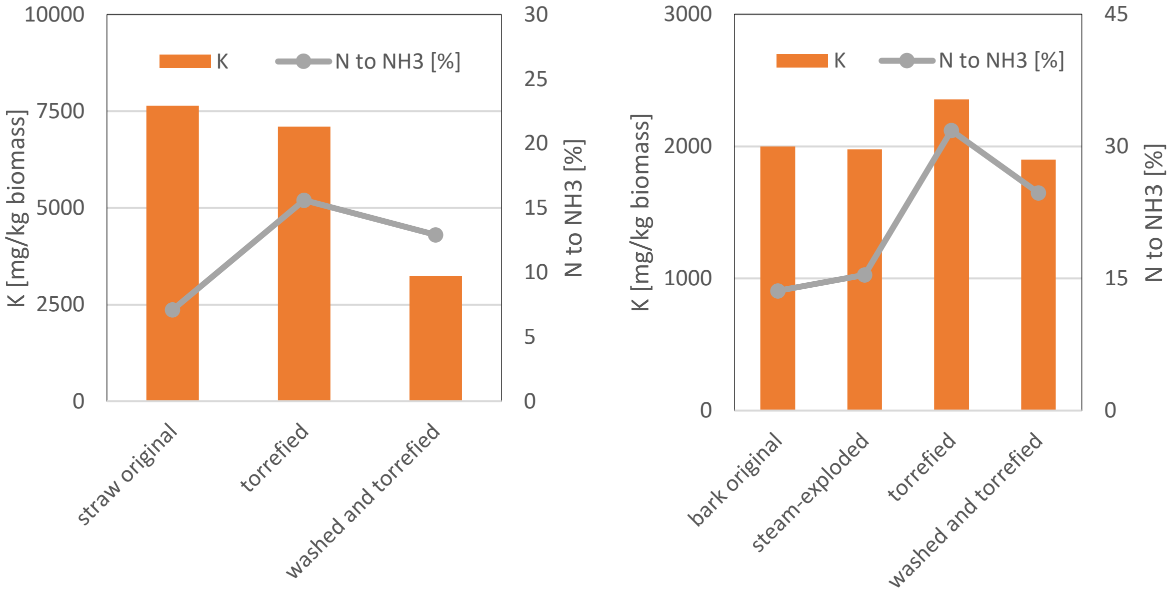

Fig. 19 Correlation between fuel-N to NH_3 conversion and amount of K in biomass.

It is possible that catalytic activity of other ash-forming elements exists in biomasses. One example could be the effect of iron since iron-based catalysts are also used for the industrial synthesis of ammonia. The concentrations of such trace elements are often low, however, so it is difficult to investigate their catalytic effects, especially in a heterogeneous system such as biomasses.

The effects of ash-forming elements which have been presented might also explain the increased conversion of volatile fuel-nitrogen to NO during combustion for the pre-treated biomasses. Since NH_3 is an important pre-cursor for NO, a higher formation of NH_3 can lead to higher NO formation when oxygen is present. Still, one has to remember that NH_3 is not the only pre-cursor. Based on the obtained data, it cannot be concluded if the total formation of pre-cursors is increasing or if it is just a shift in the ratio between NH_3 and HCN.

The methods which have been used to analyze ammonia showed good results. Still, the quantitative results must be seen with caution for different reasons. Ammonia is a reactive gas that easily sticks to surfaces. Therefore, it cannot be ruled out that some of the formed ammonia stuck on the pipe and could not reach the bottle where ammonia is collected. Losses are also conceivable in other places or that not all of the ammonia is caught in the acidic solution. As a result, it is possible that the real values are higher in most cases than the ones obtained from the experiments, but the trends can still be seen from this semi-quantitative data.

Another uncertainty with the methods which have been used is HCNO. HCNO is another nitrogen containing product from pyrolysis. In some wet chemistry analysis methods for NH_3, parts of the existing HCNO can also be converted to NH_3. It has not been tested if this is also the case for the methods that have been used for this thesis. However, the amounts of formed HCNO should be small for biomasses compared to NH_3 so uncertainties due to HCNO might be neglectable.

4.6 NO emission intensity

To evaluate the effectiveness of the pre-treatment methods, the NO emissions should also be related to the heating value of a fuel. Some fuels with higher NO emissions might be better due to higher heating values. A higher heating value means more efficiency in heat and power production, which means a lower fuel demand and thus lower total NO-emissions. Heating values which are shown in tab. 7 were measured experimentally by a commercial laboratory. Another possibility to determine heating values is to estimate them using a modified Dulong's formula [34]:

$$HHV = 0.335\ (C) + 1.423\ (H) - 0.154\ (O) - 0.145\ (N) \qquad (11)$$

Here, (C) is the carbon content in wt%, (H) the hydrogen content, (O) oxygen content and (N) the nitrogen content. The estimated heating values based on elemental analysis are also shown in tab. 7. Generally, the estimated heating values are similar to the measured heating values, implying that the modified Dulong's formula is a good approach for the investigated fuels. Estimating heating values has the advantage that it is easy to also get approximate heating values for only volatile matter and char without any elaborate experimental setups.

Tab. 7 Estimated and measured heating values

	measured HHV [MJ/kg]	estimated HHV [MJ/kg]	est. HHV volatiles [MJ/ kg]	est. HHV char [MJ/kg]
straw original	15.8	14.9	15.7	10.7
torrefied	16.4	15.4	16.3	12.1
washed + torrefied	16.4	16.2	16.1	16.5
bark original	17.4	17.6	16.0	23.9
steam-exploded	18.2	18.3	16.2	25.1
torrefied	20.5	18.8	15.4	26.0
washed + torrefied	20.3	19.8	16.2	27.5

Heating values increase as a result of torrefaction. For straw the difference is rather small between the torrefied sample and the original one. Torrefied bark on the other hand has a more than 10% higher heating value compared to its untreated equivalent. Most of the energy in straw is bound to the volatile matter. Heating values for the char are low since the chars of the straw samples contain a lot of ash-forming matte. The volatile part of bark samples has similar heating values to those of the volatiles of straw. The char of the bark, on the other hand, has a much higher heating value.

Fig. 20 shows the emission intensities for all samples, describing how much NO is emitted during combustion in 10% oxygen atmosphere per unit of obtained heat. Comparing those emission intensities with NO-emissions shown in chapter 4.3, one can see some differences. In terms of total NO-emissions, all samples except the steam-exploded bark had worse results than the untreated biomasses. Looking now on emission intensities, only the torrefied samples have worse results. Especially the torrefied bark has a much higher emission intensity than original bark. Washed + torrefied bark has a slightly lower emission intensity than original bark. The torrefied bark has only a slightly higher, and the washed + torrefied bark has a slightly lower emission intensity than original bark. Only steam-exploded bark shows again clear differences with a more than 20% lower emission intensity than untreated bark.

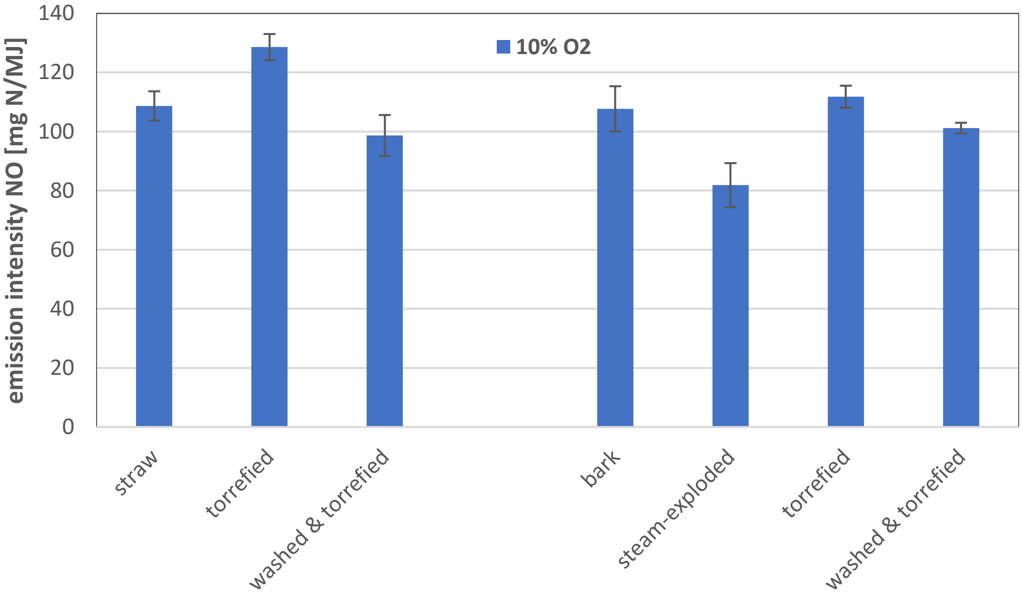

Fig. 20 The ratio between NO emissions and the amount of carbon in the biomass in 10% O_2 at 850 °C.

Fig. 21 shows the emission intensities for only pyrolysis and char combustion. For the char combustion, all pre-treated samples have a lower emission intensity than their untreated equivalent. For torrefied straw it is only slightly lower. But washed + torrefied straw for example has a 40% lower emission intensity than the original straw during char combustion. The pre-treated bark samples all have a 20-35% lower emission intensity than untreated bark. For pyrolysis on the other hand, the opposite effect can be observed. Only steam-exploded bark shows a lower emission intensity. All other pre-treated samples have higher emission intensities. The values of the torrefied samples are 30% higher than those of the untreated ones. However, exact values for emission intensities in fig. 21 have to be treated carefully since the heating values hare are only estimated. Still, the results show that pyrolysis products seem to be the major challenge for the pre-treated biomasses.

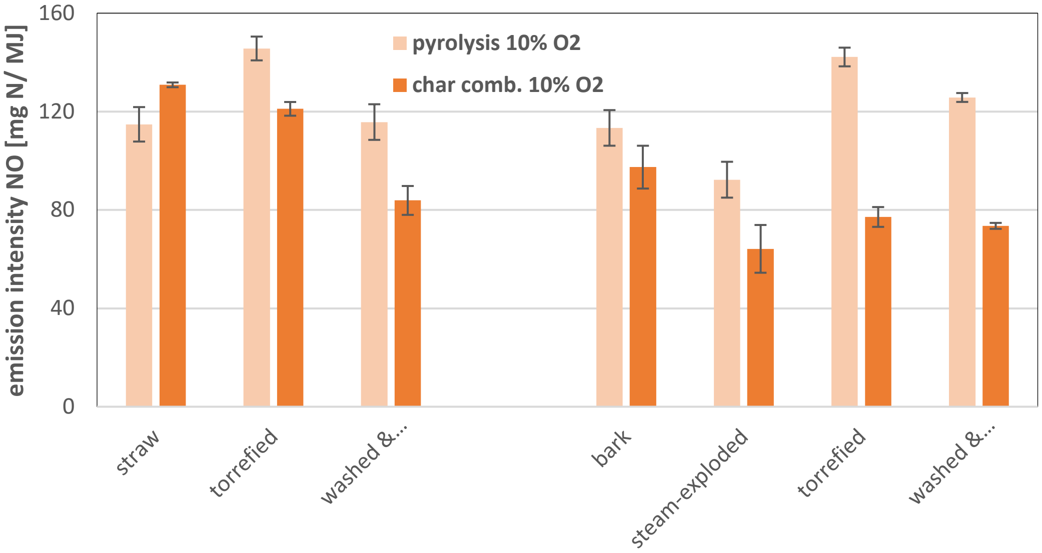

Fig. 21 The ratio of NO from pyrolysis to the amount of volatile carbon and of NO from char combustion to the char-carbon in 10% O_2/N_2 at 850 °C.

4.7 NO emissions in different atmospheres

In real combustion processes, oxygen is usually not the only reactive species in gas phase. The main products of the combustion of hydrocarbons are carbon dioxide and steam and both are able to participate in the combustion process as reactants and not only as combustion products. Hence, also other reactants than O_2 can have an influence on the NO emissions. Fig. 22 shows NO emissions for pyrolysis and char combustion of the biomasses in 3% O_2, 3% O_2/15% CO_2 and 15% CO_2. It can be seen that adding CO_2 to the reactor reduces NO emissions both during pyrolysis and char combustion. When only CO_2 is present and no oxygen, only very little NO is formed.

The slightly lower values for the release of NO from pyrolysis in O_2/CO_2 might be explained by other reactions that might occur between nitrogen containing intermediates with CO_2 or by a lower probability that those intermediates will interact with oxygen and will be oxidized. One can also see, that even when no oxygen is present, small amounts of NO are released during pyrolysis. This can also be observed during pyrolysis in pure nitrogen which means that a small amount of nitrogen must be released directly as NO from the fuel without intermediate steps. The lower emissions during char oxidation in the O_2/CO_2 mixture can be explained by the mixture with only CO_2. Fig. 23 shows the concentrations of CO and NO in the flue gas during combustion of a bark sample in 15% CO_2/N_2. Small amounts of NO are formed during pyrolysis, but almost nothing is emitted during char combustion.

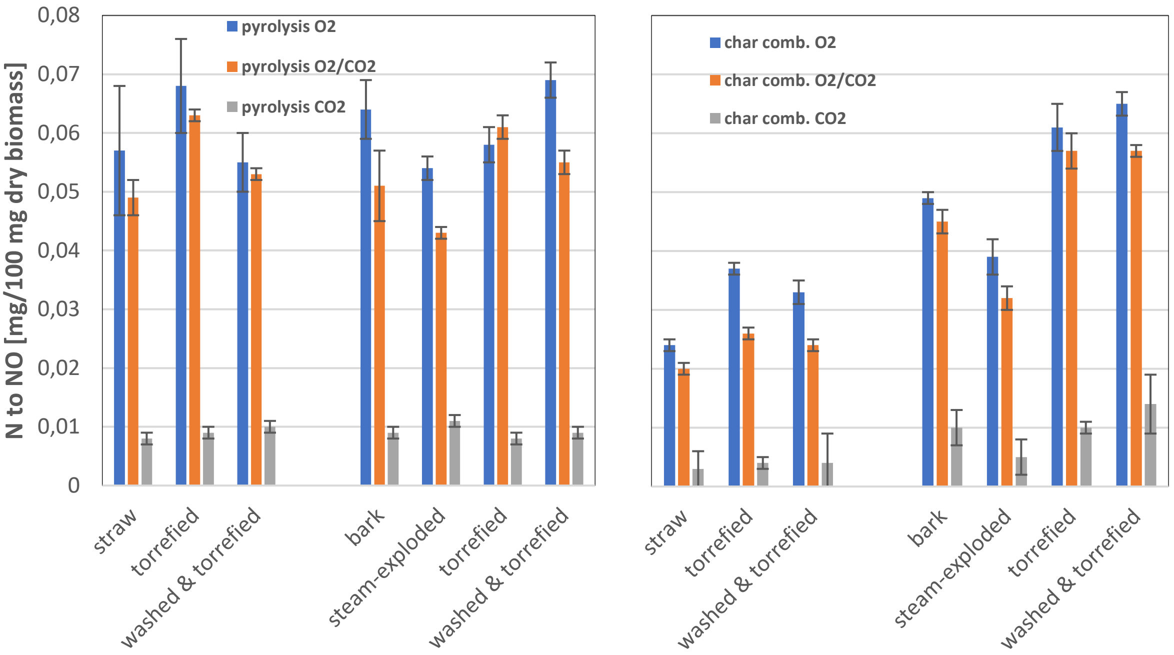

Fig. 22 NO emissions during pyrolysis and char combustion in 3% O_2, 3% O_2/15% CO_2 and 15% CO_2 at 850 °C.

Only in the end of the char combustion a NO peak appears. The peak starts to rise at the same time when CO is decreasing. This is a strong indicator for the reaction between CO and NO. One explanation could be that NO is produced all the time, but it won't be released because a big part is reduced by the char carbon before it can leave the particle and the reactor. In the end there is almost no char remaining which could reduce NO to N_2. Similar observations could be made for all fuels which have been tested.

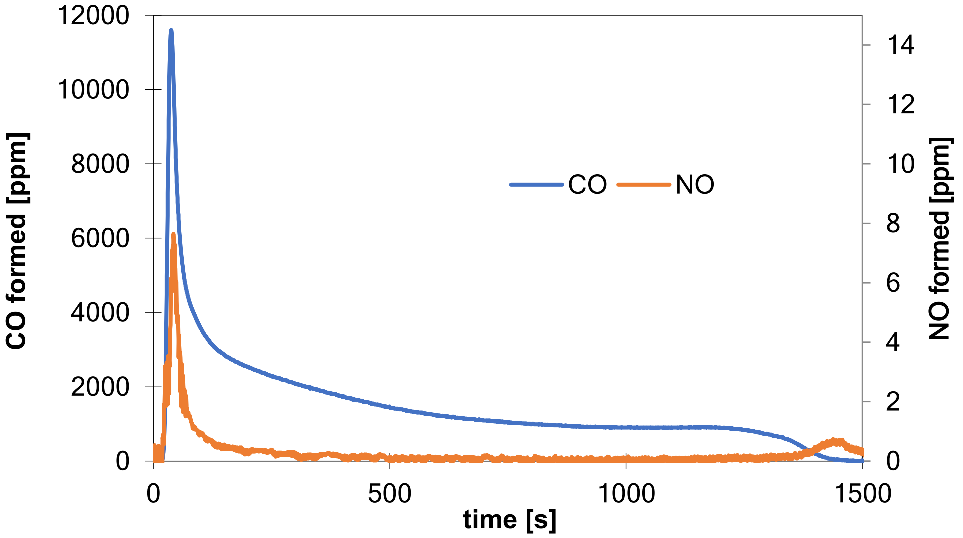

Fig. 23 CO and NO concentrations during combustion of bark in 15% CO_2/N_2 at 850 °C.

Fig. 24 presents the NO emissions for combustion in 3% O_2 and 3%O_2/15% H_2O. As with CO_2, decreased NO emissions during pyrolysis can also be observed when steam is mixed into the 3% oxygen atmosphere. The change is more significant as compared to the mixture with CO_2, which might indicate that steam is more likely to react with intermediate products or also with NO. The behavior during char combustion showed relatively large differences between the straw samples and bark samples. While the conversion of char-N to NO is reduced for the bark samples, all straw samples have higher emissions during char combustion in the O_2/H_2O mixture compared to only O_2. An explanation for this behavior could not be found yet.

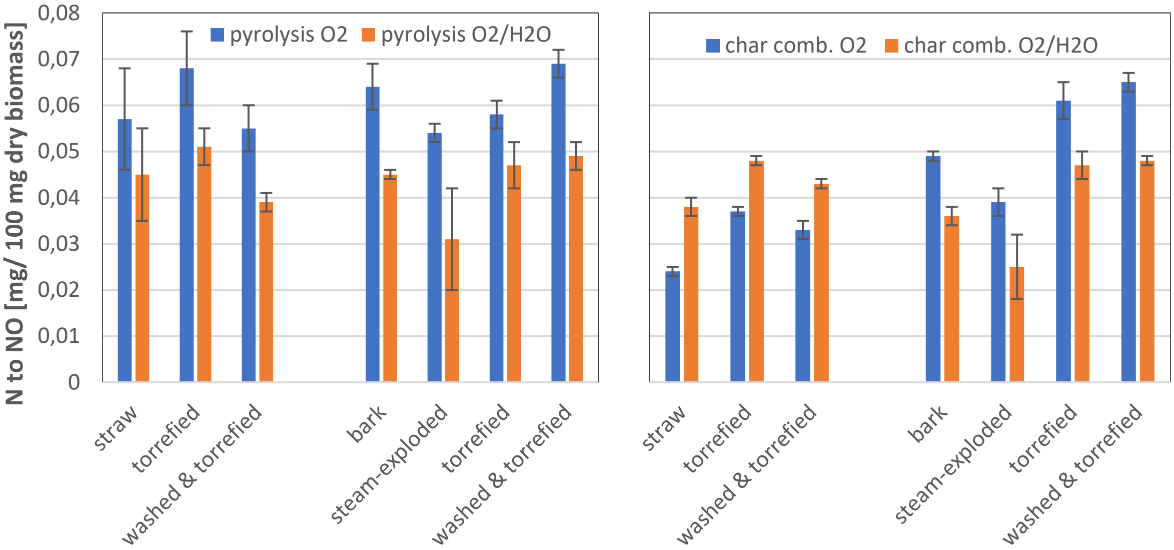

Fig. 24 NO emissions during pyrolysis and char combustion in 3% O_2 and in 3% O_2/15% H_2O at 850 °C.

Fig. 25 and 26 show concentrations curves of NO during combustion of straw and bark in 3% O_2, 3% O_2/15% CO_2 and 3% O_2/14.5% H_2O. It can be seen, that the two biomasses behave quite different in those atmospheres. For instance, the reaction time and NO emissions are almost the same when straw is combusted in 3% O_2 or in the O_2/CO_2 mixture. The combustion time of bark, on the contrary, is much shorter when CO_2 is added compared to only O_2. Also, the NO emissions are increasing during char combustion with time which is not the case for straw. When steam is added, the curves look quite different compared to the ones with only oxygen. For both straw and bark, the concentrations are much lower during pyrolysis. However, the behavior during char combustion differs again for those two biomasses. For bark the reaction time is shorter when steam is added. Straw on the other hand has a longer combustion time in the mixture with steam.

Based on the obtained data it is difficult to find explanations for the observed behavior. Further investigations are necessary, to get a better picture about the occurring reactions and reaction products and also how they differ for different biomasses and might be influenced by different biomass structures, chemical compositions and catalytic effects. Furthermore, the various biomasses should also be tested in mixtures containing O_2, CO_2 and H_2O all together.

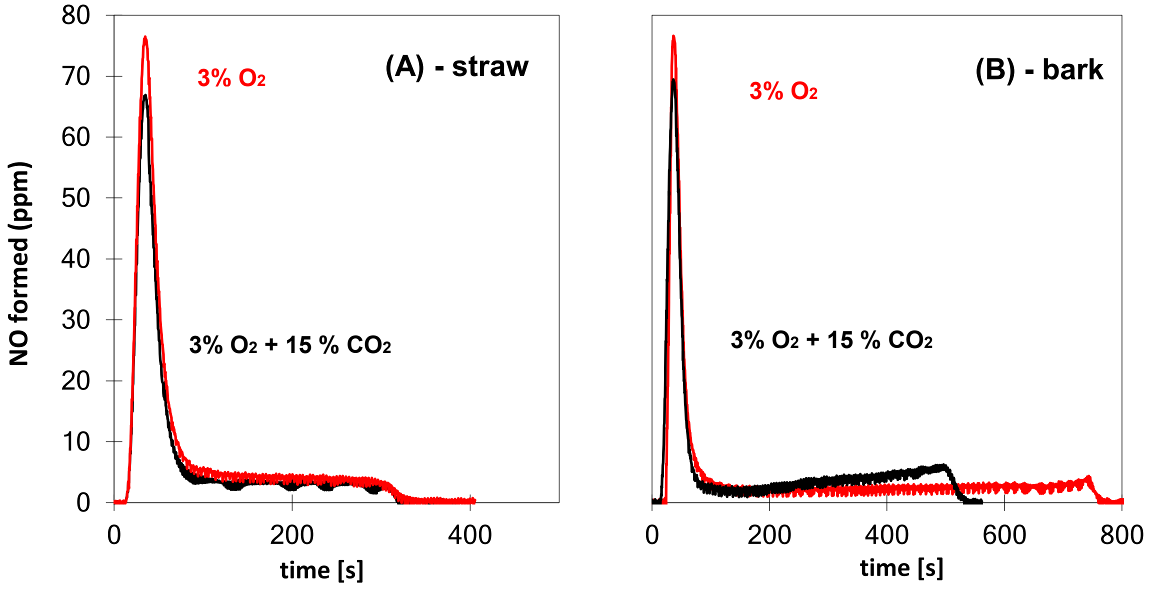

Fig. 25 NO concentrations during combustion in 3% O_2 and in 3% O_2/15% CO_2 at 850 °C.

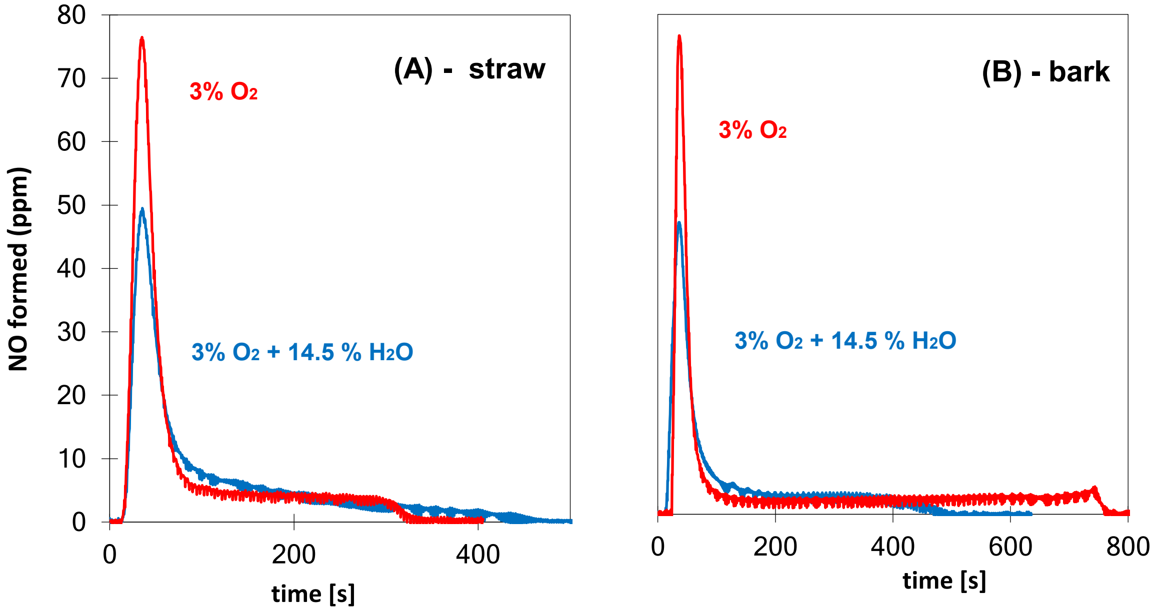

Fig. 26 NO concentrations during combustion in 3% O_2 and in 3% O_2/14.5% H_2O at 850 °C.

4.8 Black liquor

In the thesis, also black liquor, which can be viewed as a treated biomass, is investigated. The main focus was here, to test the applicability of the NH_3 analysis method on experiments with black liquor and to compare results with those from the tested biomasses.

In general, combustion behavior of black liquor differs from other biomasses since the black liquor contains only the lignin, it has a higher moisture content and because of the inorganic chemicals coming from the pulping process. Tab. 8 shows the chemical composition for the black liquor which has been used for the experiments. The values have been taken from the Åbo Akademi data base. Black liquor has a lower carbon content, hydrogen content and nitrogen content as compared to many other biomasses. Sulfur and sodium contents are high due to inorganic additives from the pulping process.

Experiments with black liquor under controlled conditions are rather difficult to perform in the single particle reactor. In some cases, black liquor swells significantly during conversion which only allows to use small sample amounts in the reactor. Additionally, the lower content of organics leads to a short combustion time, which makes it challenging to obtain meaningful results. Fig. 27 shows the NO concentration curves for the combustion in different atmospheres (compare chapter 4.6). The curves look quite different compared as to the other biomasses which have been tested previously. The shorter reaction times and the lack of a clear transition from pyrolysis to char combustion also makes it difficult to investigate both within the same experiment. Hence, only the total emissions and conversion of fuel-N to NO is shown in fig. 28. No further experiments were done within the scope of this thesis, since the focus here was on NH_3 formation.

Tab. 8 The chemical composition of the studied black liquor

	[wt% ds]		[mg/kg ds]
C	31,4	**Na**	216000
H	3,1	**K**	24000
N	0,111	**Mg**	2500
S	6,6	**Ca**	2400
		P	930

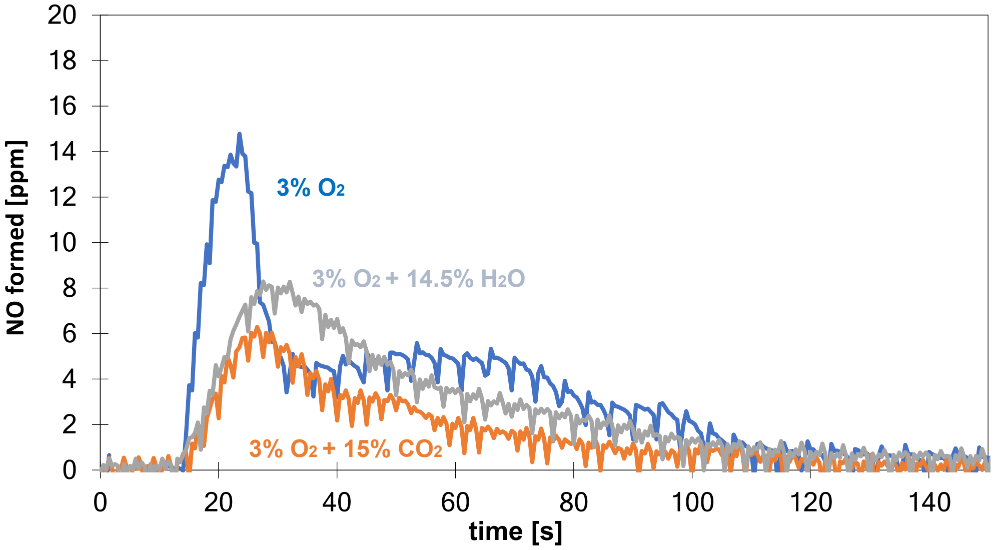

Fig. 27 NO concentrations during BL combustion in 3% O_2,3% O_2/14,5% H_2O and in 3% O_2/ 15% CO_2 at 850 °C.

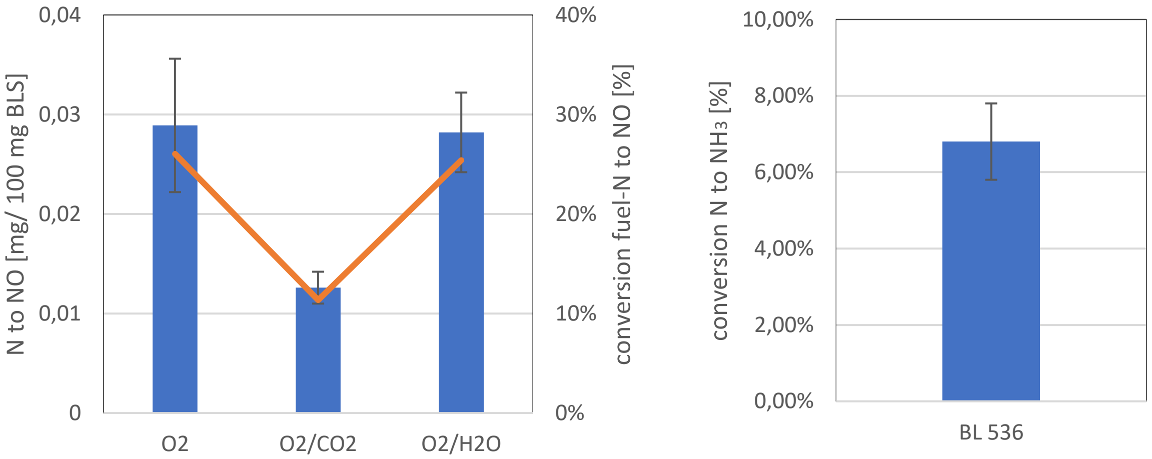

Fig. 28 NO emissions during BL combustion and conversion of fuel-N to NH_3 during BL pyrolysis.

Fig. 28 also shows the result for the NH_3-formation during pyrolysis. Around 7% of the fuel nitrogen was converted to NH_3. It could be shown that the NH_3 analysis method which has been tested for bark and straw can also be applied on black liquor. However, it is combined with much more difficulties for black liquor. Due to low fuel nitrogen concentrations, large amounts of black liquor are needed to form enough NH_3 so that it can be analyzed. In this experiment, around 6 g was used. This is time consuming since only around 50 mg of black liquor can be fed to the single particle reactor at one time. In addition, using such small amounts has the risk, that parts of the formed NH_3 are lost which leads to incorrect results. Hence, the method is rather unsuitable for black liquor and other set-ups have to be developed to investigate the nitrogen chemistry of black liquor.

5. Conclusions and outlook

In this thesis, the influence of different pre-treatments on biomass combustion has been investigated. Three different straw and four different bark samples were investigated. The main objective was to clarify, how the pre-treatment methods affect NO emissions. To measure NO emissions, pelletized samples were combusted in a single particle reactor under controlled conditions at 850 °C in different gas atmospheres containing O_2, O_2/CO_2 and O_2/H_2O. NO concentrations in the product gases were measured after the reactor and from the concentrations total emissions could be determined. The chemical compositions of the samples have also been determined using HCNS-analysis and ICP-OES for the ash-forming elements.

NO emissions varied for the different samples, but only steam-exploded bark showed a lower total NO emission compared to its untreated equivalent. However, all pre-treated biomasses showed a higher conversion of fuel-N to NO. To get a better understanding about how the pre-treatments cause higher NO emissions, the pyrolysis and char combustion stages were investigated separately. All pre-treated samples have a lower content of volatile matter. Nevertheless, the NO emissions during pyrolysis were around the same or even higher. Since NO is formed via pre-cursors during pyrolysis, a connection between effects the pre-treatments and pre-cursor formation was presumed. Hence, a new device was added to the single particle reactor to investigate the formation of NH_3, which is an important pre-cursor for NO formation. It could be shown that there is a correlation between the pre-treatments and the NH_3 formation. A correlation between calcium concentration in the biomass and the NH_3 formation, which varies for differently pre-treated sample, could be shown.

In this thesis the only pre-cursor which was studied was ammonia. In order to get a better picture about the whole process, it would be necessary to analyze other nitrogen containing pre-cursors. Especially HCN formation which competes with ammonia formation should be considered. It might also be interesting to investigate how catalytic effects on pre-cursor formation change with temperature. More structural analyses about how nitrogen is bound in the biomass could also help to complete knowledge about pre-cursor formation and might be useful for developing other pre-treatment methods to possibly lower emissions of NO and other harmful nitrogen containing combustion products.

To evaluate the pre-treatment methods regarding NO emissions, it is insufficient to only interpret the NO emissions. The pre-treated biomasses have higher heating values as compared to the untreated biomasses. Hence, it was also compared how much NO is formed per unit of heat. Heating values were measured and also estimated using a modified Dulong's equation, which gave similar values to the measured ones. Using Dulong's equation had the advantage, that heating values could also be estimated for the volatile part and the char without elaborate experiments.

Regarding emission intensities, i.e. the ratio between NO emissions and produced heat, most pre-treated fuels had better values than the untreated ones. Especially during char combustion, the pre-treated samples have much lower emission intensities. Still, the opposite effect was the case for pyrolysis and here increased emission intensities could be observed for the pre-treated samples.

6. Svensk sammanfattning

Introduktion:

Biomassa är den viktigaste energikällan i mänsklighetens historia. I och med den industriella revolutionen blev fossila energikällor mer och mer viktiga. Trenden har dock på nytt ändrat riktning och under de senaste årtiondena har användingen av biomassa ökat massivt. Det finns många orsaker till biomassans ökade användning. Både miljö- och ekonomiska frågor spelar en viktig roll. Fossila bränslen är inte hållbara eftersom användingen av fossila bränslen anses bidra till klimatförändringar på grund av förhöjd koldioxidhalt i atmosfären. Även användning av biomassa som bränsle bidrar till produktion av koldioxid, men biomassa bedöms generellt som ett klimatneutralt bränsle. Växter upptar koldioxid från atmosfären och bildar ny biomassa. Om användningen av biomassa inte överskrider växtlighetens upptag av koldioxid uppstår en jämvikt och koldioxidhalten i atmosfären ökar inte indirekt. Biomassa har även den ekonomiska fördelen att den är tillgängligt i ett stort antal länder och kan vara billigare än fossila bränslen som måste importeras från andra länder. Dessutom stiftas kontinuerligt nya lagar som kräver ett större utnyttjande av förnybar energi. Europeiska Unionen har uppsatt målet att 27% av hela energikonsumptionen ska uppfyllas av förnybara energikällor år 2030 och att utsläpp av växthusgaser skall reduceras med 40% jämfört med nivån från år 1990. Finland är ett bra exempel i och med användningen av förnyelsebara energikällor. Mellan 2011 och 2017 sjönk andelen primärenergi från fossila källor från 45% till 37%, medan andelen primärenergi från förnybara energikällor steg från 22% till 27%. Inom förnyelsebar energi är biomassa den viktigaste källan. Globalt härstammar omkring 64% av all förnybar primärenergi från biomassa.

Det finns flera alternativ för biomassas användning som energikälla. Vanligaste sättet är termokemisk omvandling genom förbränning eller förgasning. Förbränning används oftast för att utvinna värme som sen kan användas direkt eller för att omvandla värme till elektrisk ström med hjälp av ångturbiner. Förgasning däremot används för att omvandla fast biomassa till en gas genom partiell oxidation under reducerande förhållanden. Förgasningsprodukten är en gas som benämns syngas som består främst av kolmonoxid, vätgas, metan och kvävgas. Idén med förgasning är delvis produktion av gaser som kan hanteras enklare än stora mängder biomassa. Gasen kan även användas för att producera syntetiska bränslen bland annat för bilar eller andra mobila motorer.

Även om biomassans potential är stor för framtiden så finns det fortfarande många utmaningar. Ett nyckelproblem är utsläppet av kvävehaltiga avgaser från termisk konversion av biomassa, såsom NO_x eller N_2O. N_2O är en 15 gånger effektivare växthusgas än CO_2. NO_x är skadligt för miljön eftersom det bidrar till att orsaka surt regn. Följaktligen är det viktigt att skadliga kväveutsläpp minimeras. Det finns olika strategier att minska NO_x-utsläppen t.ex. genom att utnyttja vissa speciellt designade förbränningstekniker eller genom rening av avgaser. Målet med denna avhandling är att undersöka biobränslen som förbehandlats på olika sätt och undersöka hur förbehandlingsmetoderna påverkar skadliga kväveutsläpp vid termisk konversion av biomassa.

NO_x bildas vid olika steg av förbränningen. De viktigaste stegen av förbränningsprocesser är pyrolysen och koksförbränningen. Under pyrolysen frigörs lättflyktiga föreningar medan de icke-flyktiga föreningarna stannar kvar i koksen. Mängden flyktigt material varierar men brukar vara högt för biomassa. En del av bränslets kväve frigörs som flyktiga föreningar, medan andra delen stannar kvar i koksresten. En del av bränslets kväve omvandlas direkt till kvävgas men andra delar kan också omvandlas till föreningar som NH_3, HCN eller HCNO. Dessa föreningar kan agera som föregångare och i närvaro av syre kan en stor del oxideras till NO_x. Eftersom att dessa föregångare är viktiga så fokuserar arbetet även på hur olika förbehandlingsmetoder inverkar på föregångare.

I andra steget, d.v.s. koksförbränningen, sker bildning av NO_x på ett hela annat sätt. Medan NO_x-bildning under pyrolysen är en reaktion i gasfasen, så är koksförbränningen en heterogen reaktion. Bränslekvävet reagerar alltså direkt med oxidationsmedel och bildar NO_x. Allt bildat NO_x avgår inte som NO_x; NO_x kan också reagera med koks till kvävgas, eller så kan det också reduceras av CO. Dylika reaktioner sker på katalytiskt aktiva säten och följaktligen har askbildande element en viktig roll under koksförbränningen. I tidigare studier har påvisats att speciellt CaO, MgO och Fe_2O_3 inverkar på reduktion av NO_x inne i partikeln. Demineraliserad biomassa uppvisade upp till 70% omvandling av bränslekväve till NO_x medan motsvarande siffra för ursprunglig biomassan var 15-30%. I avhandlingen var det ett mål att undersöka hur förbehandlingsmetoder påverkar biomassans sammansättning, speciellt koncentrationer av askbildande element, och undersöka hur de inverkar på utsläppet av NO_x vid koksförbränningen.

Experimentellt:

I avhandlingen har halm och bark använts som biomassor. Flera olika förbehandlingsmetoder har undersökts. En av dessa förbehandlingar är torrefiering. Torrefiering är en värmebehandling i frånvaro av syre. Flyktiga ämnen avgår från biomassan och det resulterande bränslet har vanligtvis en högre energitäthet än det ursprungliga bränslet. Den andra förbehandlingsmetoden var en kombination av tvättning och torrefiering. Under tvättningen sätts biomassan i en tank med vatten och värms upp under en timme vid 50 °C. Torrefiering sker sedan efter att biomassan har torkats till en vattenhalt på 15%. Bark torrefierades vid 230 °C och halm vid 250 °C. Den tredje förbehandlingsmetoden, ångexplosion, (eng. steam-explosion), användes för bark. Ångexplosion är en teknik där biomassan utsätts för höga temperaturer och vattenånga under högt tryck för att göra fibrerna tillgängliga för reaktioner.

Samtliga prov pulveriserades och pulvren pressades till pellets med en massa på 100 mg. Dessapellets brändes sedan i en så kallad enpartikelreaktor under välkontrollerade förhållanden. Reaktorn består av en kvartsglasreaktor inne i en ugn som kan uppvärmas till önskad temperatur. De flesta experimenten genomfördes vid 850 °C. Förbränningsgasen tillförs från bottnen och från sidorna av reaktorn. Utanför reaktorn finns analysatorer som kan mäta koncentrationerna av NO, CO, CO_2, O_2 och SO_2 med ett tidsintervall på 0,5 sekunder. Genom integration av koncentrationskurvorna erhåller man totala massan och kan beräkna andelen bränslekväve som har oxiderats till NO. Dessutom användes en ny metod, där avgasen bubblades genom en vätska som bestod av 1 M HCl, så att all NH_3 från avgaserna kunde absorberas och förbli som NH_4^+ i lösningen. Detta gjordes för att bestämma andelen NH_3 som bildades under pyrolysen och därmed kunna påvisa hur förbehandlingar påverkar bildningen av kväveföreningar som vidare oxideras till NO_x.

Resultat:

Resultaten från enpartikelreaktorn visade att det finns skillnader i NO-utsläppen för bränslena efter olika förbehandlingar. I en gasatmosfär med 10% syre resulterade förbränning av torrefierad halm 25% högre NO utsläpp jämfört med oförbehandlad halm. Jämförelsen mellan oförbehandlad halm och tvättad + torrefierad halm visade att det finns en skillnad i konversionen av bränslekväve till NO. Konversionen av bränslekväve till NO var 30% i obehandlad halm, men nästan 40% i tvättad + torrefierad halm. Motsvarande resultat observerades för bark. Förbränning av torrefierad bark ledde till de högsta NO-utsläppen, medan förbränning av tvättad + torrifierad bark gav den högsta konversionen av bränslekväve till NO. Konversionen steg i sistnämnda fallet från 42% till 52%. Endast ett av de förbehandlade bränslena gav lägre utsläpp än motsvarande originalbränsle. Ångexploderad bark resulterade i omkring 20% mindre NO utsläpp än motsvarande obehandlad bark.

Eftersom vissa bränsleprov har mycket högre konversion av bränslekväve till NO kan man dra slutsatsen att bränslets kvävehalt inte är det enda som påverkar NO-utsläppen. Vissa prov ger högre NO-utsläpp, fastän bränslets kvävehalt är lägre. För att bättre kunna förstå detta beteende har pyrolysen och koksoxidationen beaktats skilt. För båda biomassorna är andelen NO från pyrolysen avsevärt högre än från koksoxideringen. För obehandlad halm är andelen omkring 85% och för obehandlad bark är andelen omkring 75%. Elementäranalyser gjordes efter pyrolys i kvävgas för att bestämma andelen flyktigt kväve och koksväve i bränslet. Resultaten visar att mängden NO från koksoxideringen korrelerar bra med andelen kokskväve. Torrefierad bark har den högsta andelen kokskväve och gav samtidigt de högsta NO-utsläppen under koksoxideringen. Ångexploderad bark gav i båda fallen det lägsta värdet och obehandlad bark det nästlägsta värdet. Värdena för NO-utsläppen och mängden flyktigt kväve korrelerar å andra sidan inte. För till exempel bark har alla förbehandlade bränslen ungefär 20% mindre flyktigt kväve, men det bildas ändå lika mycket NO som från torrefierad och tvättad + torrefierad bark. Endast ångexploderad bark bildar mindre pyrolys-NO, fastän konverteringen av flyktigt kväve till NO forfarande är högre än för obehandlad bark. Samma observationer kunde göras för halmproverna.

Eftersom NO-bildningen visar ett avvikande beteende betyder det att det måste finnas andra effekter som påverkas av förbehandlingen och inte bara mängden flyktigt kväve som förändras. I avhandlingen lades fokus på undersökningen av bildningen av ammoniak, som är en viktig föregångare till NO under pyrolysen. Två olika metoder användes för att analysera ammoniak. Metoderna gav liknande resultat. För båda biomassorna hade de obehandlade proven den lägsta konversionen av flyktigt kväve till ammoniak. De torrefierade proverna hade i båda fallen det högsta värdet och tvättad + torrefieread hade det nästhögsta värdet. Ångexploderad bark hade ett en något högre konvertering än vanlig bark.

I tidigare publikationer har visats att vissa askbildande element, huvudsakligen kalcium och kalium, har ett visst inflytande på bildningen av ammoniak under pyrolysen av vissa bränslen. Även i detta arbete kunde man se en inverkan av kalcium. Jämförelsen mellan kalciumhalten och konversionen av flyktigt kväve till ammoniak uppvisade en korrelation. Halm, som i allmänhet har lägre kalciumhalt än bark, bildar också mindre ammoniak. Kaliums eventuella inverkan kunde inte påvisas. För att få en ännu mer detaljerad förståelse borde man i framtiden undersöka också andra kvävehaltiga pyrolysprodukter såsom HCN, som är en viktig föregångare för pyrolys-NO. Även bildningen av N_2 skulle vara viktig att ta i beaktande för att kunna förstå kvävekemin i detalj.

Vid bedömandet av hur förbehandlingar inverkar på NO-utsläpp är det viktigt att korrelera NO-utsläppen med bränslets värmevärde. Eftersom den kemiska sammansättningen förändras efter förbehandlingen så betyder det att även värmevärdet för bränslet förändras. Värmevärdena har bestämts experimentellt men också via uppskattningar enligt en modifierad Dulong’s ekvation vilket gav liknande resultat och gjorde det möjligt att även få värmevärden för den flyktiga andelen och koksresten.

Utsläppsintensiten, d.v.s. mängden NO som bildas i och med att en viss mängd värme frigörs, visar att förbehandlingsmetoderna bidrar till lägre NO-utsläpp, fastän den totala mängden NO som frigjorts under experiment kan vara högre. Torrefierad bark, som ger högre NO utsläpp än obehandlad bark, har samma utsläppsintensitet och för tvättad + torrefierad bark är utsläppsintensiteten ännu lägre än för obehandlad bark. Även sett till utsläppsintensiteten är värdet lägst för ångexploderad bark. Det enda prov som har sämre värde sett till utsläppsintensiteten än det obehandlade bränslet är torrefierad bark.

Sett till utsläppsintensiteten kan man observera skillnader för pyrolys och koksoxidering. I koksoxideringens fall har alla förbehandlade bränslen lägre utsläppsintensitet än de obehandlade. För pyrolysen uppvisar samtliga bränslen förutom ångexploderad bark högre värden. Utsläppsintensiteten för pyrolys och koksoxidering är uppskattningar och värdena kan man därför inte betrakta som exakta. Trenden passar ändå bra ihop med resultaten som visar att förbehandlade bränslen leder till högre NO-utsläpp under pyrolysen på grund av den högre askhalten, som orsakar högre bildning av föregångare till NO.

Ytterligare en del i avhandlingen var att undersöka hur NO-utsläppen påverkas för de olika proven när vattenånga eller koldioxid tilläggs i förbränningsluften. Vattenånga och koldioxid är vanligtvis produkter från förbränningen och båda kan reagera i gaserna och påverka kvävekemin. För dessa experiment brändes proven i atmosfärer som innehöll både syre och koldioxid/vattenånga och sedan i atmosfärer utan syre med endast koldioxid eller vattenånga. Skillnader mellan halm- och barkproverna kunde observeras, speciellt för koksförbränningen då atmosfären innehöll vattenånga. Däremot kunde ingen påverkan av förbehandlingen på reaktionerna med CO och vattenånga fastställas.

I detta jobb har också svartlut, som är en behandlad biomassa, undersökts. Svartlut är en trögflytande avfallsprodukt från pappersindustrin som innehåller förutom organiskt material även större mängder oorganiska ämnen från sulfatprocessen. Motsvarande experiment som gjordes med halm och bark gjordes med svartlut. I detta fall fokuserades undersökningen främst på ammoniakbildningen. För svartlut gjordes ett experiment för att undersöka om analysmetoden fungerar också på svartlut, vilket det visade sig göra.

7. Literature

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Appendix

	original bark	**steam-exploded**	**torrefied**	**washed + torrefied**
[wt% ds]				
C	51.6	52.4	55.1	54.5
H	6.0	5.8	5.3	5.4
N	0.38	0.35	0.47	0.45
S	0.023	0.027	0.023	0.021
O	38.0	36.8	36.8	35.2
[mg/kg ds]				
Al	434	909	329	178
Ca	8880	10800	14200	13700
Cu	2.73	3.08	3.6	8.35
Fe	227	433	194	120
K	1760	1960	2010	1120
Mg	602	742	895	829
Mn	529	632	525	530
Na	148	311	109	203
P	398	450	491	436
Si	2640	4180	1490	550
Zn	124	32	178	167

	original bark	**torrefied**	**washed +torrefied**
[wt% ds]			
C	43.1	44.6	44.5
H	5.5	5.3	5.4
N	0.67	0.35	0.47
S	0.023	0.72	0.51
O	38.4	36.4	37.6
[mg/kg ds]			
Al	396	385	262
Ca	3660	4180	4100
Cu	3.37	3.13	7.36
Fe	245	233	140
K	7390	7780	3290
Mg	790	890	720
Mn	15.5	14.3	12.5
Na	160	166	277
P	760	721	575
Si	44900	49300	46900
Zn	7	8	10