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## Full Length Article

# Release of NH<sub>3</sub>, HCN and NO during devolatilization and combustion of washed and torrefied biomass

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## ABSTRACT

The influence of two different biomass pre-treatment methods (torrefaction and combined treatment of washing and torrefaction) on the formation of NO and its precursors, NH<sub>3</sub> and HCN, during combustion has been studied. Experiments were conducted in an electrically heated single particle reactor under well-controlled conditions in N<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> at 850 °C. NO concentrations of the product gases were measured during devolatilization and char oxidation, and the total amounts of released NH<sub>3</sub> and HCN were determined during devolatilization. The results show that the conversion of vol-N and char-N to NO changed due to the pre-treatments, influencing the NO emission factor (released NO/energy content) of the fuel. For torrefied straw, the NO emission factor was significantly higher than for raw straw. The change in NO formation can partly be explained by how the nitrogen contents change due to the pre-treatments: both for bark and straw, around 20% of the initial fuel-N was removed during the torrefaction; for straw, 50% of the initial fuel-N was removed during the combined torrefaction and washing. In addition, the changes in the NO formation can be explained by the release of NH<sub>3</sub> and HCN during devolatilization. The HCN/NH<sub>3</sub> ratio increased with increasing N content and decreasing H/N ratio due to the pre-treatments. The conversion of vol-N to NH<sub>3</sub> increased with increasing Ca content and decreasing K content. In general, the devolatilization of the pre-treated biomass samples resulted in a higher conversion of vol-N to NH<sub>3</sub> and HCN as compared to the raw biomasses.

## 1. Introduction

The European Union has a 32% renewable energy target by 2030 [1]. In 2018, around 50% of the primary renewable energy production in the EU was based on wood and other solid biomasses [2]. The presence of nitrogen is a concern in thermal conversion of biomass due to the formation of NO<sub>x</sub> and NO<sub>x</sub> emission regulations are becoming increasingly stricter [3]. NO<sub>x</sub> emissions can be divided into NO (> 90%), NO<sub>2</sub> and N<sub>2</sub>O [4]. Both NO and NO<sub>2</sub> are acid rain precursors while N<sub>2</sub>O is a greenhouse gas and ozone destroyer [5]. NO<sub>x</sub> formation in solid fuel combustion is a complex process which has been studied widely [3,5,6]. The fuel-N is typically divided into nitrogen released during devolatilization (vol-N) and nitrogen released during char conversion (char-N). Vol-N compounds comprise NH<sub>3</sub>, HCN, N<sub>2</sub>, NO and HCNCO. For high-rank coals, the vol-N is partly bound to tars [3]. Biomass tar-N can be observed at lower temperatures than temperatures typical of industrial biomass combustion, i.e. above 800 °C.

NH<sub>3</sub> and HCN are NO<sub>x</sub> precursors, but can also act as reducing agents to reduce NO to N<sub>2</sub>; NH<sub>3</sub> has a higher tendency to reduce NO to N<sub>2</sub> as compared to HCN [4]. Hence, the split of NH<sub>3</sub> and HCN is crucial

in order to understand and predict the formation of NO and has, as a result, been studied widely [7,8,9,10,11]. For spruce bark, NH<sub>3</sub> has been reported to be the major N-species while equal amounts of NH<sub>3</sub> and HCN have been formed during devolatilization of straw [12]. Besides the fuel type, the split is influenced by various factors such as temperature and heating rate: an increased heating rate has been shown to enhance the HCN release, while an increased particle size, i.e., a lower heating rate, has been shown to enhance the NH<sub>3</sub> release [5].

In biomass the nitrogen is mostly bound to proteins and, consequently, pyrolysis of various proteins and amino acids has been investigated. Chen et al. identified 17 different amino acids in a range of biomasses [13]. The carbohydrates in biomass (cellulose, hemicellulose and lignin) have different effects on pyrolysis of amino acids, possibly explaining why the NH<sub>3</sub>/HCN split differs for various biomasses [12]. In addition, ash forming elements such as K and Ca have been reported to show catalytic effects on the formation of HCN and NH<sub>3</sub> during devolatilization [10,14,15,16]. Potassium has been reported to promote the formation of NH<sub>3</sub> and to inhibit the release of HCN during pyrolysis of 2,5-diketopiperazine, while Ca had an enhancing effect on HCN and an inhibitory effect on NH<sub>3</sub> [15]. During the pyrolysis of proteins and

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amino acids, on the other hand, Ca showed an enhancing effect on the formation of  $\text{NH}_3$ , while it reduced the HCN formation [16]. For the pyrolysis of straw and corn cob it was found that K promotes, while Ca inhibits, the formation of both  $\text{NH}_3$  and HCN [17].

Ash forming matter also influences the nitrogen chemistry during the char oxidation. During char conversion, char-N reacts with  $\text{O}_2$ , mainly forming NO [18]. The formed NO can then be heterogeneously reduced by the char-C to  $\text{N}_2$  [19]. A study with raw and demineralized biomass showed that significantly more NO was released for demineralized biomasses as compared to raw biomasses [20]. Ca and K in the char may influence the conversion of char-N, by catalysing the reduction reaction between NO and char [21].

From the discussion above, it can be expected that fuel pre-treatment methods, such as torrefaction and washing (which influence the elemental composition) will influence the NO formation. Fuel pre-treatments, such as washing and torrefaction may be used to improve fuel quality and to reduce operating problems [22,23,24,25,26,27]. For example, torrefaction may result in a biomass with an improved grindability, a higher heating value and a hydrophobic surface. Water washing is a pre-treatment method which may partly remove harmful ash forming compounds [28,29]. Yet, little is known regarding how fuel pre-treatments for biomass influence the fate of the fuel-N [30].

In the present work, the release of  $\text{NH}_3$ , HCN and NO during devolatilization and combustion of raw, torrefied and washed and torrefied bark and straw have been investigated. The objective was to clarify how these pre-treatments influence the fate of the fuel-N.

## 2. Experimental

### 2.1. Fuels

Spruce bark and wheat straw were used in raw and pre-treated forms (raw bark = RB, raw straw = RS). The pre-treatment methods were torrefaction (torrefied bark = TB, torrefied straw = TS) and a combined treatment of washing followed by torrefaction (washed & torrefied bark = WTB, washed & torrefied straw = WTS). The fuel samples were obtained from two different pilot plants and were used as received. For the washing treatment, the biomass was water washed at 50 °C for one hour. Afterwards, it was sprayed with additional water and kept for drying until the moisture content was below 15%. For the torrefaction, the bark samples were pre-dried in a first step at 150 °C and the straw samples were pre-dried at 180 °C. In a second step the spruce bark and the straw were torrefied at 230 and 250 °C, respectively, resulting in mass yields of 65 and 69%. All fuel samples were analysed on their elemental composition with a CHNS analyser, and ICP-AES for the ash forming elements. The biomass samples were pulverized in the laboratory and were pressed to uniform pellets with a diameter of 8 mm and a mass of 100 mg.

### 2.2. Single particle reactor

The experiments were performed in an electrically heated single particle reactor (SPR) made of quartz glass (see Fig. 1) at 850 °C. In the setup, gases are fed from the bottom with a flow of 100 l/h at NTP and inert gas (nitrogen) from the sides with 120 l/h at NTP resulting in a total flow of 220 l/h. The fuel particle is put to the centre of the reactor via an insertion tube. Initially, the temperature of the particle increases rapidly. During the initial devolatilization, temperature gradients are present in the particle due to the large particle size, the heat transfer to the particle, the thermal conductivity of the particle and exothermal oxidation reactions. Note that this is typical for devolatilization of large biomass particle at high combustion temperature. Fuel particles with a uniform size were used in all experiments to minimize the effects of varying temperature gradients for different fuel samples. Concentrations of  $\text{O}_2$ , NO, CO and  $\text{CO}_2$  in the product gases were continuously measured. NO was measured using a chemiluminescence analyser, CO

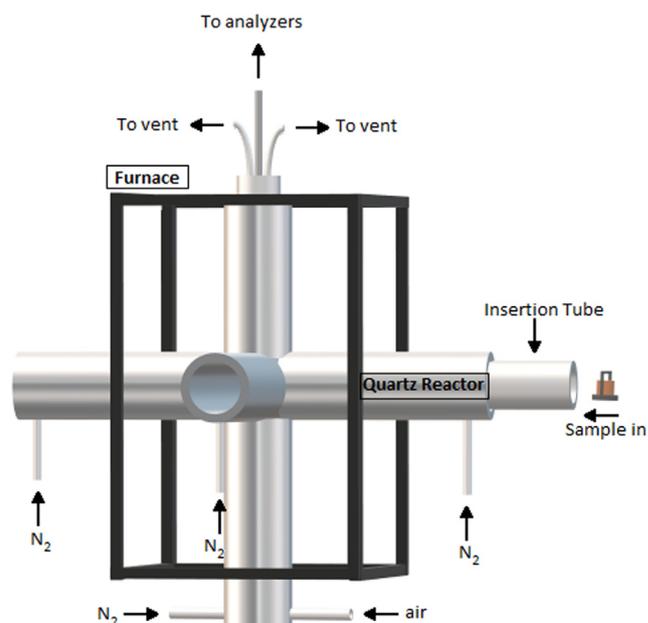


Fig. 1. Åbo Akademi single particle reactor (the black frame illustrates the electric furnace).

and  $\text{CO}_2$  using on-dispersive infrared analyser and  $\text{O}_2$  using a combined infrared + paramagnetic analyser.

The residence time from the reactor to the gas analysers was around 3 s. By comparing the fuel-C content to a carbon content based on the measured CO and  $\text{CO}_2$  signals the carbon balance can be determined: in the experiments, the carbon balance is typically higher than 90%. The reactor system has been used in several previous studies which provides more detailed experimental descriptions, e.g. [20,31,32]. In the present study, an additional setup was used for the quantification of  $\text{NH}_3$  and HCN based on a wet chemistry method. The flue gas was channelled to a 1 M HCl solution to collect  $\text{NH}_3$  in the form of  $\text{NH}_4^+$  or to a 5 wt% aqueous NaOH solution to collect HCN. Ammonium and cyanide ions were then quantified with spectrophotometry.

### 2.3. Combustion and devolatilization experiments

Two types of thermal experiments were performed: combustion and devolatilization experiments. In a combustion experiment, one single particle (placed on a sample holder (see Fig. 1)) was inserted into the heated reactor in 10 vol-%  $\text{O}_2/\text{N}_2$  and left there until the combustion ended. The reason for using an oxygen concentration of 10 vol-% in the combustion experiments was to ensure that the volatile nitrogen compounds were oxidized to NO. Each experiment was repeated three times: the deviation of NO concentrations varied < 5% for repeated runs.

Devolatilization experiments were conducted in a pure  $\text{N}_2$  atmosphere for 60 s. The experiments were conducted 30 times to collect sufficient amounts of HCN and  $\text{NH}_3$ . The experiments (i.e. 30 repetitions) were repeated twice. The distributions of nitrogen in the volatiles (vol-N) and in the char (char-N) were determined from the devolatilization experiments. The char-N was determined from the remaining nitrogen in the char and the vol-N by the difference between fuel-N and char-N.

### 2.4. Quantification of NO, $\text{NH}_3$ and HCN

Fig. 2 exemplifies the NO release curve from a devolatilization experiment in 100%  $\text{N}_2$  and from a combustion experiment in 10%  $\text{O}_2/\text{N}_2$ . The curve obtained from the combustion test includes both devolatilization and char conversion, as marked in the figure. NO concentrations

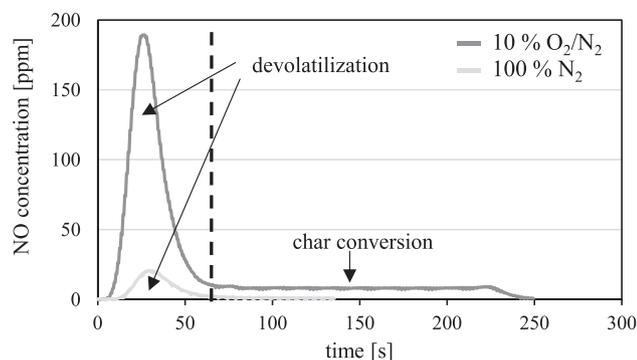


Fig. 2. NO release during combustion and devolatilization of spruce bark at 850 °C.

of the product gas increase rapidly during the devolatilization and drop rapidly after reaching a maximum after approximately 30 s. During the char oxidation, however, the NO concentrations in the product gas are much lower and on a constant level until the char oxidation has ended and the NO concentration drops to 0. The curve obtained from the devolatilization experiments in inert atmosphere only includes devolatilization as char oxidation does not take place under these conditions. The total amount of released NO during the devolatilization and during the char conversion was determined by integrating the devolatilization part and the char conversion part, respectively, while NH<sub>3</sub> and HCN were quantified by spectrophotometry.

### 3. Results and discussion

#### 3.1. Fuel composition

Table 1 gives the proximate and ultimate analysis of the fuels. The pre-treated samples have higher carbon contents, and higher heating values, as compared to the raw biomasses. The pre-treated samples have, in general, higher nitrogen contents. The difference in the ash forming matter varies dependent on the elements. For example, the torrefied samples have higher concentrations of Ca and K, although the washed and torrefied samples have lower concentrations of K, possibly explained by element-specific differences in the water solubility.

Table 1

Proximate and ultimate analysis of the fuel samples.

	RB	TB	WTB	RS	TS	WTS
Moisture, wt%	7.4	1.5	1.8	3.4	2.4	2.4
Volatile matter wt% ds, 850 °C	79.4	68.1	68.3	85.0	78.2	78.7
HHV, MJ/kg ds	19.03	20.82	20.71	16.22	16.86	16.83
Ultimate analysis, wt% ds						
C	51.6	55.1	54.5	43.1	44.6	44.5
H	6.0	5.3	5.4	5.5	5.3	5.4
N	0.38	0.47	0.45	0.67	0.72	0.51
S	0.022	0.023	0.021	0.106	0.107	0.063
O*	40.4	37.1	37.9	44.6	42.8	43.8
Ash wt% ds, 550 °C	4.0	4.9	4.4	12.3	12.9	11.9
Ash forming elements, mg/kg ds						
Si	2640	1490	550	44,900	49,300	46,900
Al	434	329	178	396	385	262
Ca	8880	14,200	13,700	3660	4180	4100
Fe	227	194	120	245	233	140
K	1760	2010	1120	7390	7780	3290
Mg	602	895	829	790	890	720
Mn	529	525	530	15.5	14.3	12.5
Na	148	109	203	160	166	277
P	398	491	436	760	721	575
Cl	110	< 80	< 80	1320	956	248

\*By difference.

Note that Table 1 presents the actual contents in each fuel sample on a dry solid basis. Fig. 3, on the other hand, shows the relative contents of the pre-treated samples compared to the initial raw samples and, thus, how much of the original elements remaining after the treatment. For TB and WTB, the relative concentrations of the major elements (C, H, N, S and O) are between 60 and 80% which is approximately proportional to the total mass loss during torrefaction. The ash forming elements behave differently. For instance, for the bark, nearly all of the Ca and Mg remained after the pre-treatments while the contents of the other ash forming elements decreased.

Fig. 4a shows the split of vol-N and char-N, and also the amount of N removed during the pre-treatment. For clarification, Fig. 4b illustrates the fate of nitrogen during pre-treatment, devolatilization and char conversion. For bark and straw, the initial splits vol-N/char-N were 69/31 and 90/10; for torrefied bark and straw, the splits were 51/30 and 60/14; and for washed and torrefied bark and straw, the splits were 53/23 and 42/10, respectively. Thus, around 20% of the initial N was lost in the pre-treatments, except for the washed and torrefied bark: almost 50% of the initial N was removed. Thus, a significant amount of nitrogen was removed due to the pre-treatments.

#### 3.2. NO release from combustion experiments

Fig. 5 shows the amount of released NO from the combustion experiments. For RB, the amount of released NO is around 4 g NO/kg fuel, which corresponds to an emission factor of 0.22 g NO/MJ. For TB, the amount of released NO increased to 4.6 g NO/kg fuel, which is around 15% higher as compared to that of RB. However, the emission factor is almost unchanged as TB has a higher heating value than RB. The amount of released NO was slightly higher for WTB than for RB, although the emission factor was slightly lower. For RS, the amount of released NO was around 3.3 g NO/kg, resulting in an emission factor of 0.20 g NO/MJ. The amount of released NO from TS was higher, 4.1 g NO/kg, which represents an increase of around 25% as compared to RS. In addition, the emission factor for TS was around 20% higher as compared to RS. WTS, on the other hand, only had slightly higher emissions, 3.4 g NO/kg, and the same emission factor as RS.

It is important to emphasize the amounts of released NO of the straw clearly do not correlate with the nitrogen contents. TS has only a slightly higher fuel-N content than RS (see Table 1), although the amount of released NO was significantly higher. The fuel-N content of WTS is around 25% lower than that of RS, although the amounts of released NO were almost identical. For the bark samples, on the other hand, the amounts of released NO correlate with the fuel-N contents. An earlier study presented by Ren et al. also reported varying trends for the NO emissions from different biomass fuels after torrefaction [30]. For instance, NO emissions during the combustion of corn straw and beech wood were much higher when the samples were torrefied, while olive residue and rice hush had much lower NO emissions when torrefied.

Fig. 6 shows the conversion of fuel-N to NO from the combustion experiments (a) and the conversion of vol-N (b) and char-N (c) during the devolatilization stage and the char oxidation, respectively. For RB, 51% of the fuel-N formed NO during the combustion. For TB and WTB, the conversion of fuel-N to NO was 45%. This can mainly be explained by that the conversion of the vol-N to NO during devolatilization decreased. The conversion of the fuel-N to NO is mainly influenced by the conversion of vol-N to NO since the majority of the NO is formed during the devolatilization stage (70% for bark and 80% for straw). Interestingly, for straw, the opposite trend can be observed as compared to bark. The pre-treated straw samples showed higher conversions of the vol-N to NO, hence also for the conversion of fuel-N to NO. For the conversion of char-N to NO, similar observations can be done for RB and RS. For both bark and straw, the torrefied samples showed the lowest conversion of char-N to NO, while the washed and torrefied samples showed the highest conversion. This observation is in line with observation from earlier studied on the char conversion of biomass

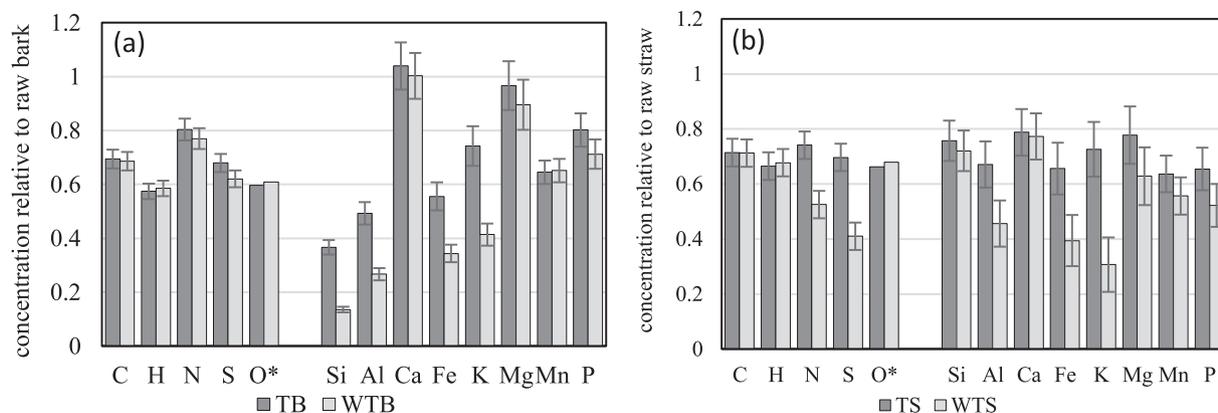


Fig. 3. Relative concentrations in pre-treated bark (a) and straw (b); 1 = concentration in untreated sample (TB = torrefied bark, WTB = washed & torrefied bark, TS = torrefied straw, WTS = washed & torrefied straw).

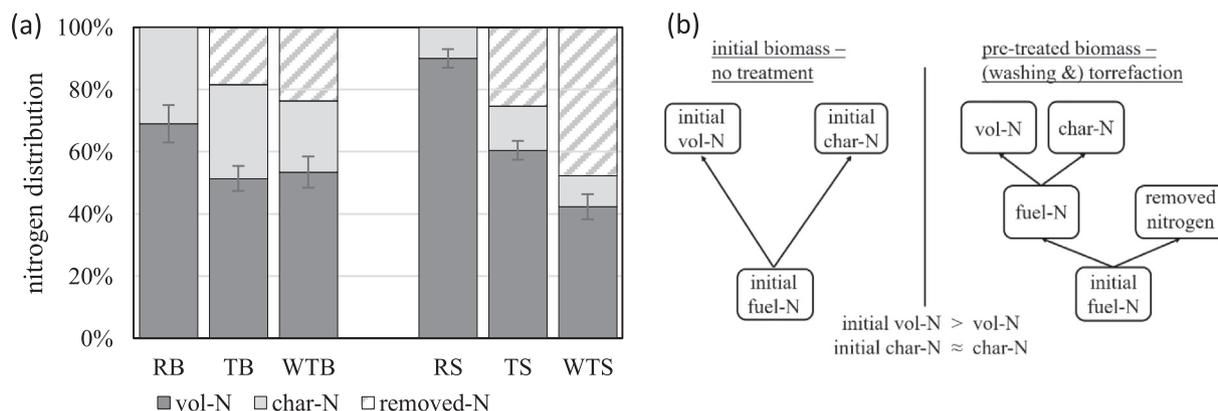


Fig. 4. Distribution of vol-N, char-N and removed-N (removed during pre-treatment) based on the fuel-N content in the raw biomass (a) and illustrative figure on the fate of initial fuel-N (b) (RB = raw bark, TB = torrefied bark, WTB = washed & torrefied bark, RS = raw straw, TS = torrefied straw, WTS = washed & torrefied straw).

[20].

In the torrefied samples, ash forming elements, e.g. K, are enriched, which might promote the catalytic reduction of NO during char oxidation. In washed and torrefied samples, however, the ash forming elements are partly leached, which might inhibit the catalytic reduction of NO to N<sub>2</sub> by the char surface.

### 3.3. Formation of NH<sub>3</sub>, HCN and NO during devolatilization

Fig. 7 shows the conversion of vol-N to NH<sub>3</sub>, HCN and NO during devolatilization at 850 °C. For RB, the conversion of vol-N to NH<sub>3</sub> was 21%, the conversion of vol-N to HCN was 8%, and the conversion of vol-N to NO was 6%. The conversion of vol-N to NO for the pre-treated bark and RB were similar. In addition, the conversions of vol-N to NH<sub>3</sub> and HCN from WTB and RB were similar as well. However, for TB an increased conversion of vol-N to NH<sub>3</sub> and HCN can be observed: 27%

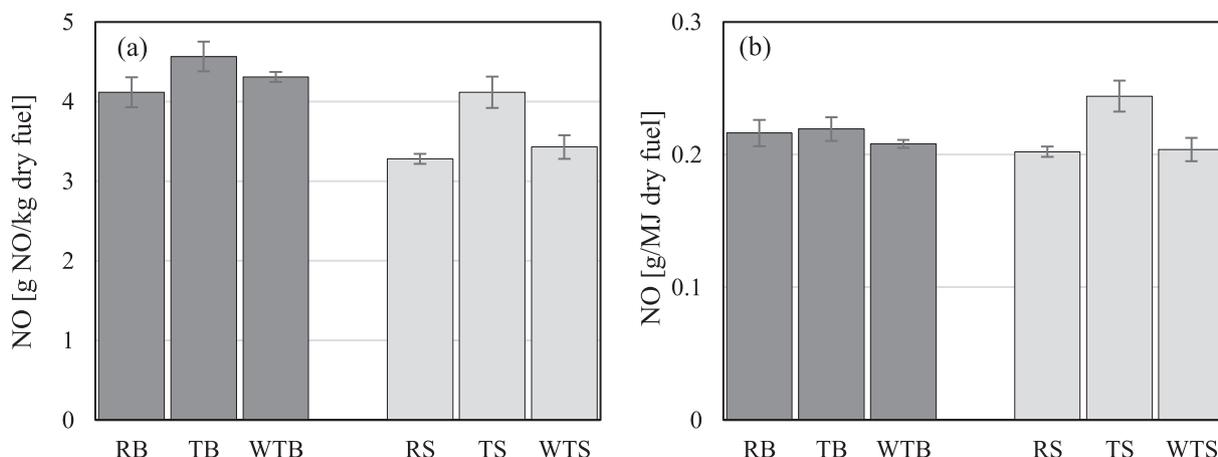


Fig. 5. NO emission based on fuel mass [g/kg] (a) and NO emission factors based on heating values of the fuel samples [g/MJ] (b) in 10% O<sub>2</sub> at 850 °C (RB = raw bark, TB = torrefied bark, WTB = washed & torrefied bark, RS = raw straw, TS = torrefied straw, WTS = washed & torrefied straw).

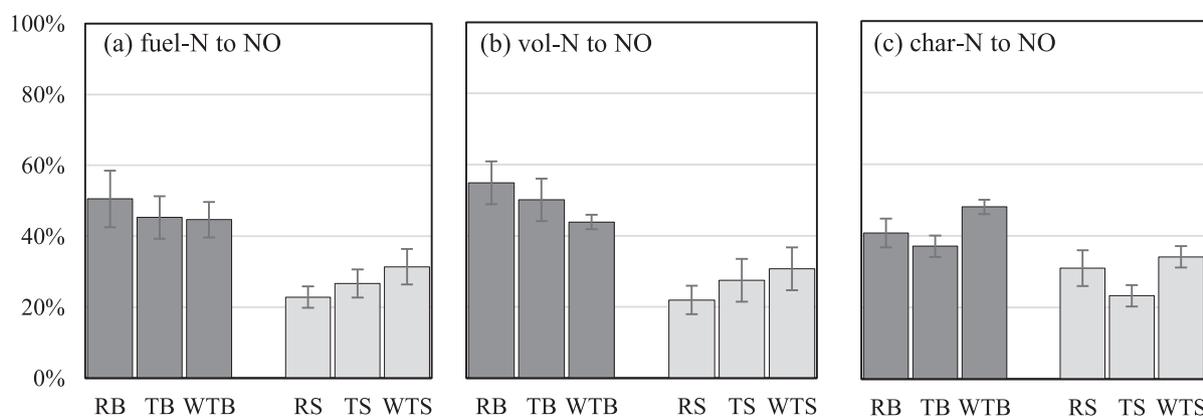


Fig. 6. Conversion of a) fuel-N to NO, b) vol-N to NO and c) char-N to NO in the combustion experiments at 850 °C (RB = raw bark, TB = torrefied bark, WTB = washed & torrefied bark, RS = raw straw, TS = torrefied straw, WTS = washed & torrefied straw).

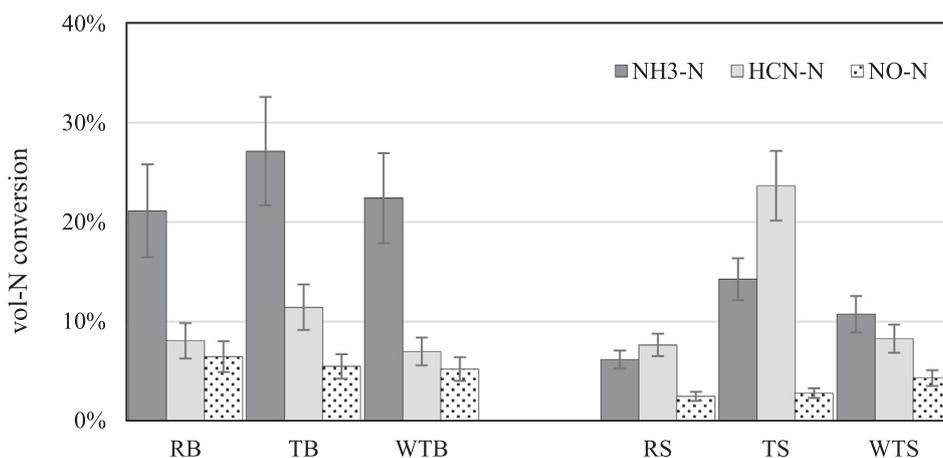


Fig. 7. Conversion of vol-N to NH<sub>3</sub>, HCN and NO during devolatilization in pure N<sub>2</sub> at 850 °C (RB = raw bark, TB = torrefied bark, WTB = washed & torrefied bark, RS = raw straw, TS = torrefied straw, WTS = washed & torrefied straw).

and 11% respectively.

For RS, on the other hand, the conversion of vol-N to NH<sub>3</sub> is in general significantly lower as compared to RB, but the conversions of vol-N to HCN are similar in both cases. The conversion of vol-N to NH<sub>3</sub> was 6%, the conversion of vol-N to HCN was 8% and the conversion of vol-N to NO was 3%. The conversions of vol-N to NO are similar for the raw and the pre-treated straw. Also, the conversion of vol-N to HCN for WTS and RS are similar while the conversion of vol-N to NH<sub>3</sub> increased to 8% for WTS. For TS, a significant increase can be observed for the conversion to NH<sub>3</sub> and HCN. The conversion of vol-N to NH<sub>3</sub> and HCN are here 14% and 24% respectively.

The results emphasize that, in general, higher amounts of NO precursors are formed during devolatilization for the pre-treated samples as compared to the raw samples. The NO formation during devolatilization, on the other hand, is similar for raw and pre-treated samples. These results help to explain the NO trends discussed previously in Fig. 5 and Fig. 6. TB forms more NH<sub>3</sub> and HCN during devolatilization and it can also be seen that the NO formation from the corresponding combustion experiment is higher. For TS, the conversion of vol-N to NH<sub>3</sub> and HCN increased significantly and so did also the NO formation in the combustion experiment. The effect of pre-cursors is further illustrated in Fig. 8, which shows the NO formation during combustion as a function of the amount of precursors formed during the devolatilization experiments. In general, more NO is formed from the samples with a higher amount of formed precursors.

As discussed previously, the split of HCN and NH<sub>3</sub> influence formation of NO in oxidizing environments. Fig. 9a shows the molar HCN/

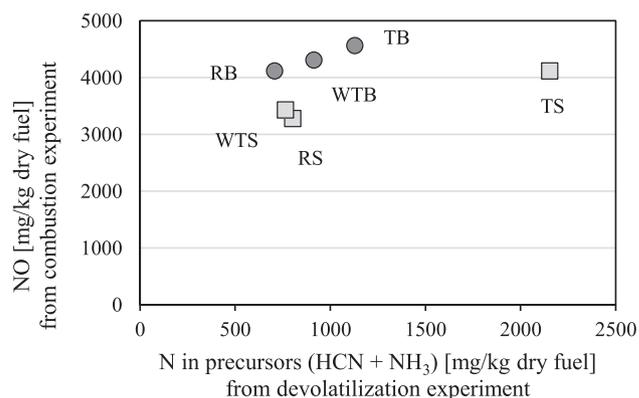


Fig. 8. Correlation between NO formation from combustion experiments in 10% O<sub>2</sub> and HCN and NH<sub>3</sub> from devolatilization experiments in pure N<sub>2</sub> (RB = raw bark, TB = torrefied bark, WTB = washed & torrefied bark, RS = raw straw, TS = torrefied straw, WTS = washed & torrefied straw).

NH<sub>3</sub> ratio for the various samples as a function of the fuel-N content, while in Fig. 9b the ratio is plotted against the molar H/N ratio in the fuel. These results are in line with results from an earlier study reporting that an increased fuel-N content and decreased H/N ratio resulted in a higher HCN/NH<sub>3</sub> ratio [7]. This can partly be explained by the formation mechanisms of HCN and NH<sub>3</sub>. For instance, HCN can partly be converted to NH<sub>3</sub> when hydrogen is present. Hence, biomass pre-treatments have a significant influence on the HCN/NH<sub>3</sub> ratio when

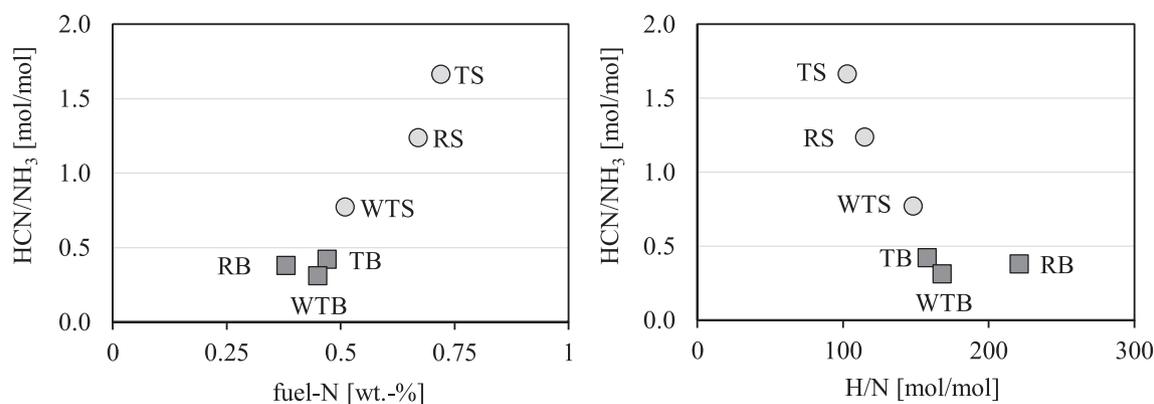


Fig. 9. Molar HCN/NH<sub>3</sub> ratio versus fuel-N (a) and molar H/N (b) (RB = raw bark, TB = torrefied bark, WTB = washed & torrefied bark, RS = raw straw, TS = torrefied straw, WTS = washed & torrefied straw).

the H/N ratio changes during the pre-treatment.

An additional explanation for the increased HCN/NH<sub>3</sub> ratios could be variations in the amount of the biomass components cellulose, hemicellulose and lignin. It has been shown, that lignin can lead to polymerization reactions during pyrolysis between cellulose, hemicellulose and proteins [33]. A plausible results from this is that heterocyclic nitrogen more likely forms HCN than NH<sub>3</sub>. A recent study investigated effects of torrefaction on cellulose, hemicellulose and lignin at different temperatures [34]. It was shown, that large parts of the hemicellulose are removed, while most of the cellulose and lignin is left, thus lignin is enriched. This might lead to an increased polymerization and hence to increased HCN formation. This might also explain why the HCN/NH<sub>3</sub> ratio is so much higher in straw as compared to bark, since the lignin content of straw is significantly higher than the lignin content of bark [35,36].

As mentioned above, ash forming matter also may influence the formation of NH<sub>3</sub> and HCN. However, opposing effects of K and Ca have been reported. Fig. 10 shows the conversion of vol-N to HCN and NH<sub>3</sub> as functions of the calcium content (a) and the potassium content (b). Generally, the changes in HCN formation are rather small as compared to the changes in Ca and K contents, with TS as the only exception, and no obvious trend can be observed. For NH<sub>3</sub>, on the other hand, the results imply that more NH<sub>3</sub> is formed in the samples with a higher calcium content and a lower potassium content.

#### 4. Conclusions

The formation of NH<sub>3</sub>, HCN and NO during devolatilization and

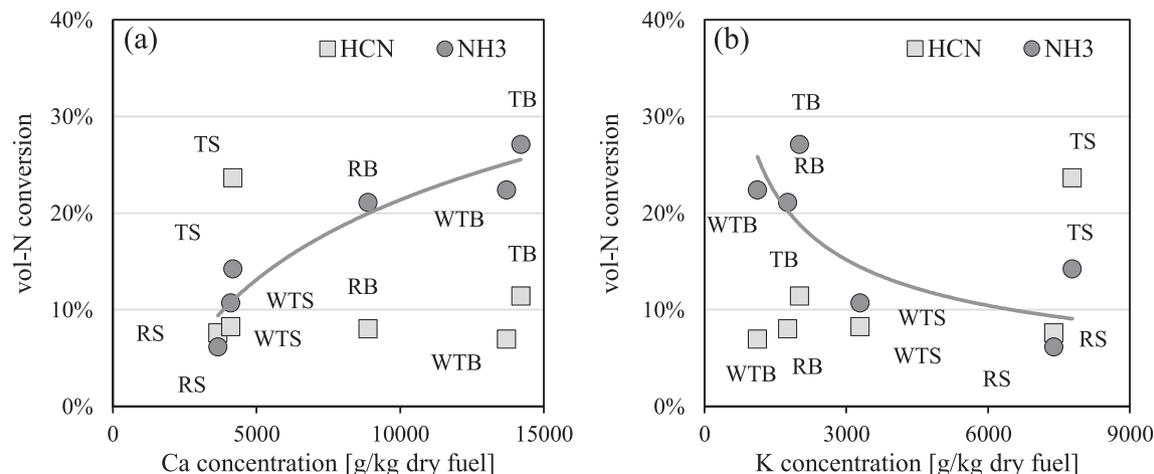


Fig. 10. Conversion of vol-N to HCN and NH<sub>3</sub> versus Ca (a) and K (b) concentration in the fuel samples (RB = raw bark, TB = torrefied bark, WTB = washed & torrefied bark, RS = raw straw, TS = torrefied straw, WTS = washed & torrefied straw).

combustion of raw, torrefied and washed and torrefied biomass fuels has been studied. The following conclusions can be drawn:

- The pre-treatments resulted in a higher conversion of vol-N to NH<sub>3</sub> and HCN as compared to the raw biomass fuels. The highest amounts of NH<sub>3</sub> and HCN were formed for torrefied straw.
- NO conversion was lower for pre-treated bark samples than raw bark, although the NO emission factor did not differ significantly.
- NO conversion was higher for pre-treated straw samples in comparison with raw straw. Torrefied straw had a significantly higher emission factor than raw straw.
- The contents of ash forming elements, the fuel-N content and the molar H/N ratio was significantly influenced by the pre-treatments. The results support the hypothesis that the HCN/NH<sub>3</sub> ratio increases with increasing N content and decreasing H/N ratio. In addition, the conversion of vol-N to NH<sub>3</sub> increased with decreasing K content and increasing Ca content.

#### CRediT authorship contribution statement

**Daniel Schmid:** Conceptualization, Methodology, Investigation, Writing - original draft. **Oskar Karlström:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition. **Patrik Yrjas:** Writing - review & editing, Resources, Funding acquisition.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## References

- [1] EU. Conclusion of the European Council, 2030 climate and energy policy framework. October 2014, revised in 2018.
- [2] Pelkmans L. European Union – 2018 update Bioenergy policies and status of implementation; 2018. <https://www.ieabioenergy.com/iea-publications/country-reports/2018-country-reports/>.
- [3] Glarborg P, Jensen A, Johnsson J. Fuel nitrogen conversion in solid fuel fired systems. *Prog Energy Combust Sci* 2003;29:89–113.
- [4] Mladenovic M, Dakic D, Nemoda S, Paprika M, Komatina M, Repic B, et al. The combustion of biomass – the impact of its types and technologies on the emission of nitrogen oxide. *Hemijaska Industrija* 2016;70:287–98.
- [5] Hansson K-M, Samuelson J, Tullin C, Åmand L-E. Formation of HNCO, HCN and NH<sub>3</sub> from the pyrolysis of bark and nitrogen-containing model compounds. *Combust Flame* 2004;137:265–77.
- [6] Giuntoli J, de Jong W, Verkooyen A, Pietrowska P, Zevenhoven M, Hupa M. Combustion characteristics of biomass residues and biowastes: fate of fuel nitrogen. *Energy Fuels* 2010;24:5309–19.
- [7] Anca-Couce A, Sommersacher P, Evic N, Mehrabian R, Scharler R. Experiments and modelling of NO<sub>x</sub> precursor release (NH<sub>3</sub> and HCN) in fixed-bed biomass combustion conditions. *Fuel* 2018:529–37.
- [8] Becidan M, Skreiberg Ø, Hustad J. NO<sub>x</sub> and N<sub>2</sub>O precursors (NH<sub>3</sub> and HCN) in pyrolysis of biomass residues. *Energy Fuels* 2007:1173–80.
- [9] Leppälähti J. Formation of NH<sub>3</sub> and HCN in slow-heating-rate inert pyrolysis of peat, coal and bark. *Fuel* 1995;9:1363–8.
- [10] Liu H, Yi L, Hu H, Xu K, Zhang Q, Lu G, et al. Emission control of NO<sub>x</sub> precursors during sewage sludge pyrolysis using an integrated pretreatment of Fenton peroxidation and CaO conditioning. *Fuel* 2017;195:208–16.
- [11] Hansson K-M, Åmand L-E, Habermann A, Winter F. Pyrolysis of poly-L-leucine under combustion-like conditions. *Fuel* 2003;82:653–60.
- [12] Ren Qiangqiang, Zhao Changsui. Evolution of fuel-N in gas phase during biomass pyrolysis. *Renew Sustain Energy Rev* 2015;50:408–18. <https://doi.org/10.1016/j.rser.2015.05.043>.
- [13] Chen Hanping, Si Yaohui, Chen Yingquan, Yang Haiping, Chen Deming, Chen Wei. NO<sub>x</sub> precursors from biomass pyrolysis: distribution of amino acids in biomass and Tar-N during devolatilization using model compounds. *Fuel* 2017;187:367–75. <https://doi.org/10.1016/j.fuel.2016.09.075>.
- [14] Ren X, Zhao C. NO<sub>x</sub> and N<sub>2</sub>O precursors (NH<sub>3</sub> and HCN) from biomass pyrolysis: interaction between amino acid and mineral matter. *Appl Energy* 2013;21:170–4.
- [15] Zhou J, Gao P, Dong C, Yang Y. Effect of temperature and mineral matter on the formation of NO<sub>x</sub> precursors during fast pyrolysis of 2,5-diketopiperazine. *Energies* 2018:629.
- [16] Yi L, Liu H, Lu G, Zhang Q, Wang J, Hui H, et al. Effect of mixed Ca/Fa additives on nitrogen transformation during protein and amino acid pyrolysis. *Energy Fuels* 2017;31:9484–90.
- [17] Ren Q, Zhao C, Wu X, Liand C, Chen X, Shen J, et al. Effect of mineral matter on the formation of NO<sub>x</sub> precursors during biomass pyrolysis. *J Anal Appl Pyroly* 2009;85:447–53.
- [18] Winter F, Wartha C, Hofbauer H. NO and N<sub>2</sub>O formation during the combustion of wood, straw, male waste and peat. *Bioresour Technol* 1999:39–49.
- [19] Pereira F, Beer J, Gibbe B, Hedley A. NO<sub>x</sub> emissions from fluidized-bed coal combustion. *Symp (Int) Combust* 1975;15:1149–56.
- [20] Karlström Oskar, Perander Magnus, DeMartini Nikolai, Brink Anders, Hupa Mikko. Role of ash on the NO formation during char oxidation of biomass. *Fuel* 2017;190:274–80. <https://doi.org/10.1016/j.fuel.2016.11.013>.
- [21] Ulusoy B, Wu H, Lin W, Karlström O, Li S, Song W, et al. Reactivity of sewage sludge, RDF and straw chars towards NO. *Fuel* 2019;236:297–305.
- [22] Chen Dengyu, Mei Jiaming, Li Haiping, Li Yiming, Lu Mengting, Ma Tingting, Ma Zhongqing. Combined pretreatment with torrefaction and washing using torrefaction liquid products to yield upgraded biomass and pyrolysis products. *Bioresour Technol* 2017;228:62–8. <https://doi.org/10.1016/j.biortech.2016.12.088>.
- [23] Davidsson K, Korsgren J, Pettersson J, Jäglid U. The effects of fuel washing techniques on alkali release from biomass. *Fuel* 2002;81:137–42.
- [24] Tan H, Wang S. Experimental study of the effect of acid-washing pretreatment on biomass pyrolysis. *J. Fuel Chem. Techn.* 2009;37(6):668–72.
- [25] Batidzirai B, Mignot A, Schakel W, Junginger H, Faaij A. Biomass torrefaction technology: techno-economic status and future prospects. *Energy* 2013;62:196–214.
- [26] Rentizelas A, Li J. Techno-economic and carbon emission analysis of biomass torrefaction downstream in international bioenergy supply chains for co-firing. *Energy* 2016;114:129–42.
- [27] Uslu A, Faaij A, Bergman P. Pre-treatment technologies, and their effect on international bioenergy supply chains logistics. Techno-economic evaluation of torrefaction, pyrolysis and pelletisation. *Energy* 2008;33:1206–23.
- [28] Turn S, Kinoshita C, Ishimura D. Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass Bioenergy* 1997;12:241–52.
- [29] Jenkins B, Bakker R, Wei J. On the properties of washed straw. *Biomass Bioenergy* 1996;10:177–200.
- [30] Ren Xiaohan, Sun Rui, Meng Xiaoxiao, Vorobiev Nikita, Schiemann Martin, Levendis Yiannis A. Carbon, sulfur and nitrogen oxide emissions from combustion of pulverized raw and torrefied biomass. *Fuel* 2017;188:310–23. <https://doi.org/10.1016/j.fuel.2016.10.017>.
- [31] Karlström O, Wu H, Glarborg P. Influence of H<sub>2</sub>O on NO formation during char oxidation of biomass. *Fuel* 2019:1260–5.
- [32] Karlström O, Hupa L. Conversion of biomass char: Oxidation rates in mixtures of O<sub>2</sub>/CO<sub>2</sub>/H<sub>2</sub>O. *Energy* 2019;181:615–24.
- [33] Yuan S, Zhou Z, Li J, Chen X, Wang F. HCN and NH<sub>3</sub> released from biomass and soybean cake under rapid pyrolysis. *Energy Fuels* 2010;24:6166–71.
- [34] Chen D, Gao A, Cen K, Zhang J, Cao X, Ma Z. Investigation of biomass torrefaction on three major components: hemicellulose, cellulose and lignin. *Energy Convers Manage* 2018;169:228–37.
- [35] Kapoor M, Panwar D, Kaira G. Bioprocesses for enzyme production using agro-industrial wastes: technical challenges and commercialization potential. *Agro-Industrial Wastes as Feedstock for Enzyme Production*. Elsevier Inc.; 2016.
- [36] Räisänen T, Athanassiadis D. Basic chemical composition of the biomass components of pine, spruce and birch; 2013.