Influence of pre-treatment of straw biomass and additives on the release of nitrogen species during combustion and gasification

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Abstract

The aim of this study is to investigate how pre-treatment of herbaceous straw biomass for ash control affects the release of nitrogen species during combustion and gasification. To comprehend the formation of NO and its precursors, NH_3 and HCN, the release of these species was investigated and compared under both combustion and gasification-like conditions at 950 °C. The effects of various upgrading methods, such as torrefaction, water-leaching, a combination of leaching and torrefaction, and $CaCO_3$ addition, were studied. The assessment of nitrogen release was divided into two consecutive conversion steps – devolatilization/pyrolysis and ash/char reactions. The release of nitrogen is highly dependent on the reaction conditions. For instance, the emissions of NO from the combustion conditions (3 vol% O_2) for all fuel samples were, on average, six times higher than under gasification conditions (14.5 vol% H_2O and 5 vol% CO_2). The emissions of NO from the combustion and gasification of torrefied biomass were, on average, 20% higher than those from raw biomass. Water-leaching had a suppressing effect on NO formation during char conversion. Approximately 62% of the char-N formed NO for raw and torrefied material, whereas only 26% to 35% was formed for pre- or postwashed samples. The effect of the applied pre-treatment approaches on the release of nitrogen was particularly significant during char conversion. Increasing calcium and decreasing potassium content had catalytic effects, mainly on the conversion of volatile-N to NH_3. The Ca-doped biomass feedstock showed approximate 10% increase in volatile-N to NH_3 conversion compared to the source material.

Keywords

Air pollutant emissions; Ammonia; Biomass upgrading; Combustion; Gasification; Hydrogen cyanide; NO_x precursors

Full-length article (Word count: 6809)

Nomenclature

Abbreviations

char-C	Char carbon
char-N	Char nitrogen
fuel-N	Fuel nitrogen
IR	Infrared
kN	Kilonewton
M	Molar concentration
N	Nitrogen
N-content	Nitrogen content
Nl	Norm litre
NO_x	Nitrogen oxide
removed-N	Removed nitrogen
SPR	Single particle reactor
To	Torrefied
To-WL	First torrefied, then water-leached
To-WL + A	First torrefied, then water-leached plus 2 wt% $CaCO_3$ additive
vol(atile)-N	Volatile nitrogen
WL	Water-leached
WL-To	First water-leached, then torrefied

Symbols and units

T_G	Torrefaction grade in wt%
T_{iso}	Isothermal temperature in °C
wt%	Weight percentage
vol%	Volume percentage

1. Introduction

In recent years, there has been a significant increase in demand for renewable and climate-friendly energy. Renewables are gradually replacing fossil energy sources (oil, natural gas, lignite and hard coal) as well as nuclear energy. Consequently, the utilization of biomass for electricity and sustainable fuel production has become increasingly attractive. The production of a wide range of biomass waste streams offers enormous potential for generating renewable energy, and thermal conversion is widely considered one of the most suitable approaches [1,2].

However, gasification and combustion of non-recyclable waste and biomass waste is associated with several potential environmental risks, economic challenges, and operational challenges caused by high-temperature corrosion, bed agglomeration, fouling and slagging, and pollutant emissions. When utilizing waste fuels or biomass with high nitrogen contents, it is crucial to address potential harmful NOx emissions alongside [3,4]. While nitrogen may appear to be a minor constituent of biomass, it is a major area of concern, particularly due to the potential for high NOx emissions from thermal conversion processes. Nitrogen oxides are responsible for causing significant environmental and health impacts including the promotion of acid rain, the generation of ozone through NO_x conversion in the lower troposphere and contributing to smog formation [3–5]. The composition of NO_x can be divided principally into three major components: roughly 90% of nitrogen oxides are emitted in the form of NO, while the remaining portion is emitted in the form of NO_2 and N_2O [6].

Nitrogen is an essential nutrient that plays a crucial role in plant function, as it is a key element of amino acids. It provides the primary component for the formation of the building blocks of plant enzymes and proteins [7]. The form in which nitrogen is bound in the biomass influences the release of nitrogen during thermal conversion [8–11]. Fuel-N can be converted to molecular nitrogen or gas phase pollutants and pollutant precursors such as ammonia, hydrogen cyanide, and oxides of nitrogen (NO_x) during high-temperature gasification. The nitrogen present in fuel, or fuel-N, can be subdivided into two categories: nitrogen released during devolatilization (volatile-N), and nitrogen released during char conversion (char-N). Volatile-N compounds usually include NO, N_2, NH_3, N_2O, HCN, HNCO, and tar-N [12]. The distribution of nitrogen compounds during devolatilization depends on several factors, such as the temperature and ash composition [12–17]. Ammonia is a reducing agent for NO_x reduction. The main global reduction reaction can be described as:

$$4\ NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

The mechanism in Eq. 1 underlines the correlation between the ammonia concentration in the fuel and the formation of NO. The higher the ammonia concentration, the more dominant the de-NO_x mechanism as demonstrated by Koger et al. [18]. There are several detailed NO_x reduction mechanisms available in the literature, such as those presented in references [19] and [20]. Despite being quite complex, the detailed mechanisms for nitrogen oxides formation in biomass combustion have been well described so far [21], however, more investigations are needed under gasification conditions in order to fully understand and compare the formation process of N-species with regard of both conditions. In order to clarify the practical value of this research work, the role and effects of nitrogen compounds are briefly introduced in the following. According to Table ***1***, thermal NO_x, prompt NO_x and fuel NO_x are the three different mechanisms for NO formation [22].

Table 1: NO formation mechanisms during combustion and gasification after [22].

	Mechanism/reaction	**Condition**
Thermal (Zeldovich)	$O + N_2 \rightarrow NO + N$	$T > 1300$ °C
	$N + O_2 \rightarrow NO + O$	Excess of O_2
	$N + OH \rightarrow NO + H$	
Prompt (Fenimore et al.)	$CH + N_2 \rightarrow HCN + N$	Fuel rich zone
	$CH_2 + N_2 \rightarrow HCN + NH$	
Fuel	Conversion of fuel-N	Residence, nitrogen fraction in fuel

When N_2 in air is oxidized at high temperature ($T > 1300$ °C), thermal NO forms. Since gasification is carried out under fuel-rich conditions and occurs typically at $T \leq 1100$ °C, thermal NO_x can be neglected in comparison to fuel-NO_x for biomass gasification applications [23]. In contrast, prompt NO_x depends weakly on temperature and is formed by hydrocarbon fragments attacking N_2 near to the flame zone [24]. Consequently, the prompt mechanism occurs primarily in rich hydrocarbon flames. Lastly, fuel-NO_x is produced by the oxidation of fuel-N. As mentioned earlier, NH_3 and HCN are the main gaseous nitrogenous products formed during the combustion or gasification of biomass, and they serve as precursors for NO [25]. The conversion of fuel-N is a multistep process and begins with the decomposition of biomass material through pyrolysis, which releases a portion of fuel-N as tar-N [13,21]. The tar-N is then converted into volatile-N compounds such as NH_3, HCN, and minor amounts of HNCO through tar-cracking. Hansson et al. [25] reported that a substantial amount of fuel-N remains in the char matrix in the form of char-N during pyrolysis. The oxidation of char with oxygen primarily produces NO. The oxidation of NO-precursors NH_3 and HCN in the gas phase leads to the production of NO and N_2. The NO formed initially can undergo reduction within the pore of char particles through either heterogeneous or homogeneous reactions catalyzed by both surface of the char and inorganic components in the presence of carbon monoxide, as mentioned in [26,27]. The conversion of fuel-N to NH_3 in fluidized bed air gasification is typically high, while the conversion of fuel-N to HCN is very low. Lowering the operating pressure and increasing the gasification temperature result in higher HCN concentrations [28]. In addition, lower heating rates and larger particle sizes tend to produce more NH_3 production, whereas higher heating rates promote increased HCN production. Based on the previously described mechanisms, it is apparent that gas composition and particle size significantly impact N-chemistry and the resulting products. Consequently, it is crucial to conduct and optimize biomass combustion or gasification applications under conditions that closely resemble the intended final application.

The catalytic effect of fuel ash is of great interest, especially since the presence of compounds of Ca, Mg, K, Fe, and Na may catalyze the reduction of NO and NO_2 [6,29,30]. Thermochemical gasification of biomass usually takes place in a low-oxygen environment (air/fuel ratio <1). The fate of fuel-N under gasification conditions has been studied in detail, and fuel-N is liberated mainly as ammonia, hydrogen cyanide, molecular nitrogen, or as aromatic compounds, and a smaller part of the nitrogen is retained in solid char [31,32]. It has been demonstrated that ammonia is the dominant N-containing compound in the gas phase during biomass gasification, resulting in an increased generation of NO_x [33]. This implies that precise measurements of NH_3 levels must be a crucial factor in regulating NO_x emissions. While various studies have thoroughly discussed the mechanisms of NO_x formation in combustion processes [34], the mechanisms under gasification conditions remain poorly defined.

Based on the catalytic effects originating from the ash, it is reasonable to assume that pre-treatment of fuels, such as torrefaction and water-leaching, which alter the chemical composition, would impact NO_x emissions. This is because the initially released NO_x reacts directly with the char surface and char-NO_x reactions are catalysed by ash compounds. There are only a few studies that have investigated the effect of pre-treatments on fuel-N release, and the underlying mechanisms are not yet fully understood [12,35]. Pre-treatment of herbaceous biomass feedstocks and additives are used to alter various ash-related issues in fluidised bed gasification, such as bed agglomeration, fouling and slagging, and high-temperature corrosion [36]. This may influence the release of harmful NO_x and the pre-cursors NH_3 and HCN as well. Detailed understanding of the nitrogen chemistry and its transformation mechanism during biomass combustion or gasification is necessary in order to effectively reduce N-related pollution risk factors [37]. Ash-forming matter influences the nitrogen chemistry; several studies reported that Ca and K may catalyze the reduction reaction between NO and char [16,38–40].

Hence, this research aims at investigating the impact of different fuel pre-treatments and additives utilized for ash control to elucidate their influence on nitrogen fate during thermal conversion. It is essential to comprehend the impact of pre-treatment on biomass to utilize biogenic residues efficiently for thermal energy conversion. Biochemical looping gasification leads to the discharge of pollutants like nitrogen oxides and sulfur oxides. Therefore, it is necessary to take measures to reduce emissions. Biomass pre-processing has the potential to optimize supply chains by making biogenic residue usable, which would otherwise be difficult due to issues such as ash-related corrosion [36,42]. However, biomass upgrading should only be considered if it does not cause other problems, such as increased formation of NO_x. If upgrading leads to the production of more nitrogen or sulfur oxides, it is important to take this into account when optimizing the combustion process. This could be achieved, for instance, by implementing a flue gas cleaning system.

The experiments were conducted under both combustion and gasification-like conditions, and the outcomes are presented in this work. It should be noted that ash-related concerns in biomass gasification are generally thought to be analogous to those in combustion due to inorganic constituents [41]. However, the specific behavior of new biomass fuels under gasification conditions is not well-defined. The situation may differ for nitrogen chemistry since the formation of NO_x precursors is primarily determined by the oxygen partial pressure during the process. The current study indicates that the upgrading of biomass has a significant influence on NO emissions. The pre-processing methods yielded increased conversion of volatile-N to NH_3 in comparison to the untreated source material. Additionally, calcium and potassium exhibited catalytic effects on the volatile-N to NH_3 conversion, with calcium decreasing and potassium increasing the conversion rates, thereby corroborating the initial hypothesis.

2. Methodology

2.1. Fuels and pre-treatment methods

Commercially purchased (Futtermittel Louven, Erftstadt, Germany) wheat straw was investigated in raw, torrefied, water-leached and $CaCO_3$-doped forms. Wheat straw is a substantial agricultural biomass waste product worldwide, with an annual global production of 529 million tons [59]. The precise chemical composition of the fuel may vary depending on the source of the wheat straw, but it is generally similar. The pre-treatment methods were thermal treatment (torrefaction = To), water-leaching (= WL), and combinations of both steps (first water-leached, then torrefied = prewashed = WL-To, and first torrefied, then water-leached = postwashed = To-WL). Furthermore, a sample containing 2 wt% $CaCO_3$ was prepared by adding it to the torrefied and subsequently water-leached sample (= To-WL + A) to investigate the previously mentioned catalytic impacts of calcium.

For the torrefaction treatment, a dry torrefaction method was applied. Firstly, the biomass was pre-dried at 110 °C for 3 h in argon. The feedstock was subsequently torrefied at 250 °C for 1 h under the same atmospheric conditions, resulting in a torrefaction grade of T_G = 27.8 wt%. The torrefaction grade was determined by calculating the percentage of mass loss of torrefied biomass in comparison to the initial mass (untreated material). This can be expressed mathematically as shown in Equation (1):

$$T_G = m_{initial\ (wt\%)} - m_{torrefied\ (wt\%)} \tag{1}$$

The water-leaching treatment involved washing 50 g biomass twice with 0.5 l deionized water at room temperature for 1 h each time. After each washing step, the washing water was removed via vacuum filtration. The biomass was subsequently rinsed with small quantities of deionized water and left to dry inside a fume hood for 24 h. All fuel samples were milled and sieved to a diameter of 0.56 mm in order to improve further analytical investigations. The elemental composition was determined with a CHNS analyser and an ICP-OES after the fuel was mixed with lithium borate, heated up to 1000 °C and subsequently dissolved in HCl. The chloride content was analysed with ion chromatography, approx. 150 mg of sample was shaken vigorously in 10 mL Milli-Q water for 24 h, followed by centrifugation and filtration. For the experiments the fuel was pressed to uniform, cylindrical pellets (the applied pressure was fixed to 49 kN) with a diameter of 8 mm and a mass of 200 mg (for the quantification of NO) and 400 mg (for the quantification of both NH_3 and HCN), respectively. The ash amount was gravimetrically determined by ashing the (pre-treated) feedstock samples in air until the mass remained unchanged (36 h, 550 °C).

2.2. Single particle reactor

A single particle reactor (SPR), constructed of quartz glass and heated electrically (refer to Figure 1), was utilized to investigate the combustion and gasification behavior of straw samples. The quartz tube reactor was inserted in a heated ceramic furnace. The reaction gases were fed with a constant flow rate of 100 Nl h^{-1} from the bottom of the reactor and inert gas (nitrogen) from the sides of the reactor with a flow of 120 Nl h^{-1}, resulting in a total flow of 220 Nl h^{-1}. The product gases left at the top of the reactor. The combustion and gasification experiments were performed throughout the study at T_{iso} = 950 °C, which represents the setpoint for the SPR furnace wall temperature. The temperature was set to 950 °C for comparability with similar research focus, as previous studies [36,42] had focused on inorganic species rather than nitrogen species. Sample pellets were placed in the center of the quartz reactor via an insertion tube. A decisive advantage of the SPR is that only one single pellet is sufficient per measurement to fully investigate the devolatilization and char conversion or ash reaction. The size of the sample pellet was kept constant in order to minimise potential effects of varying temperature gradients for different pre-treated fuel samples. Concentrations of the (product) gases were measured continuously: CO, CO_2, O_2 and NO. O_2 was monitored to track the progress of the reaction and measured using a combined IR + paramagnetic analyzer. CO and CO_2 were measured using a non-dispersive IR analyzer, and NO was measured using a chemiluminescence analyzer. Both carbon species were monitored in order to compare the fuel-C content to a carbon content based on the measured CO_2 and CO signals, and the carbon balance was typically observed to be higher than 90%. In regards to the calculation of mass balances for N recovery, any difference to 100% was considered to be N_2 or nitrogen bound in tars, as these fractions cannot be determined. Therefore, the fitness of the setup was checked by calculating the carbon balance, as was done in [12]. The residence time from the reactor to the gas analyser was short, less than three seconds. In the heated reactor the residence time was approximately 1 s, and after the reactor, when the gases were rapidly cooled, the residence time was approximately 2 s.

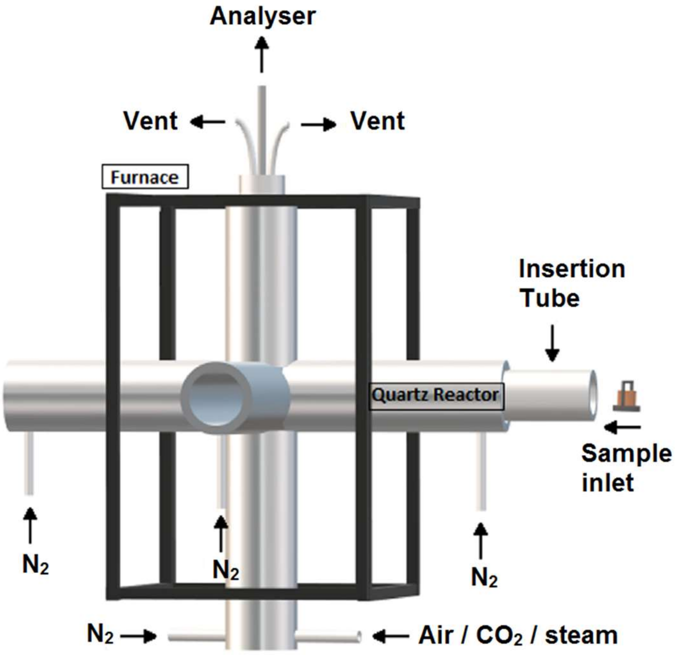

Figure 1: A schematic illustration of the single particle reactor (SPR) used in the experiments. The black frame represents the electrically heated furnace (T_{iso} = 950 °C). Modified after Schmid et al. [12].

The SPR reactor has been used in several previous studies. A more detailed description can be found elsewhere [12,31,43,44]. Both the process temperature and gas atmosphere can be precisely adjusted, allowing accurate measurement for the monitoring of NO produced. A continuous on-line gas analysing system ensured that the gas concentrations were constantly measured throughout the experiment in order to track the progress of the initial devolatilization and subsequent char conversion reactions. Another advantage of the SPR is that the whole quartz glass reactor was evenly maintained at a constant process temperature. The main limitations of the SPR are attributed to the single particle pellet itself, as the temperature of the particle increased shortly after being inserted to the center of the reactor. Note that during devolatilization, temperature gradients are typically present in the biomass particle due to the thermal conductivity, the exothermal oxidation reactions, and the large particle size. In this research, a special setup for collecting both NH_3 and HCN was used, based on a wet chemistry method, analogous to [12]. For the analysis of released NH_3, the flue gas was directed to an ice-cooled 1 M HCl solution in order to collect NH_3 in form of NH_4^+. HCN was collected in an ice-cooled 1 M NaOH solution. Note that the flue gas was directed into a gas wash bottle that contained either HCl or NaOH solution, and ice-cooling ensured condensation of the product gases. The solutions were filtrated afterwards to isolate impurities such as char residues. Both ammonium and cyanide ions were quantified by spectrophotometry, and based on the quantitative ion analysis, the amount of released NH_3 and HCN could be determined.

2.3. Gasification, combustion and devolatilization experiments

Three types of thermal experiments were performed: gasification, combustion and devolatilization experiments. The devolatilization experiments were conducted in 100 vol% N_2, the gasification experiments in 5 vol% CO_2, and in a mixture of 14.5 vol% H_2O and 5 vol% CO_2, while the combustion experiments were done in 3 vol% O_2. Based on a previous study [45], an oxidation concentration higher than 3 vol% accelerates char oxidation and decreases fuel-N conversion to NO, in accordance with thermal de-NO_x mechanisms. Hence, a lower oxygen concentration was selected since the conversion of fuel-N was the focus of this study. Furthermore, experiments with 5 vol% CO_2 and 3 vol% O_2 as well as 14.5 H_2O, 5 vol% CO_2 and 3 vol% O_2 were conducted. These gas compositions were chosen as intermediate mixtures to draw conclusions about each gas component and specifically, the interaction between the gas mixtures on the nitrogen chemistry. Nitrogen was used as the balance gas for each experiment.

For each experiment, a single pellet was placed on a glass sample holder and inserted into the reaction zone, set at 950 °C. The pellet was kept in the reactor until the combustion or gasification ended. To estimate the error dispersion, the standard deviation of the emitted NO concentration was determined for each experiment, which was repeated three times. The constant deviation of the NO concentration during the sequence of trials indicated a homogeneous sample composition.

The devolatilization experiments were performed in pure N_2 for two minutes and the residual char was collected in order to determine the remaining N-content via CHNS analysis. Both char-N and volatile-N were determined from the devolatilization experiments, while the amount of removed nitrogen was determined by CHNS analysis of each pre-treated sample.

To determine the release of NH_3 and HCN during devolatilization, each experiment was repeated with 400 mg pellets twenty times. This ensured that sufficient amounts of absorbed NH_3 and HCN were present in the solutions (HCl or NaOH) for subsequent chemical analysis.

2.4. Analysis and quantification of NO

Figure 2 displays the results of the untreated straw combustion, gasification, and devolatilization experiments, in terms of NO release.

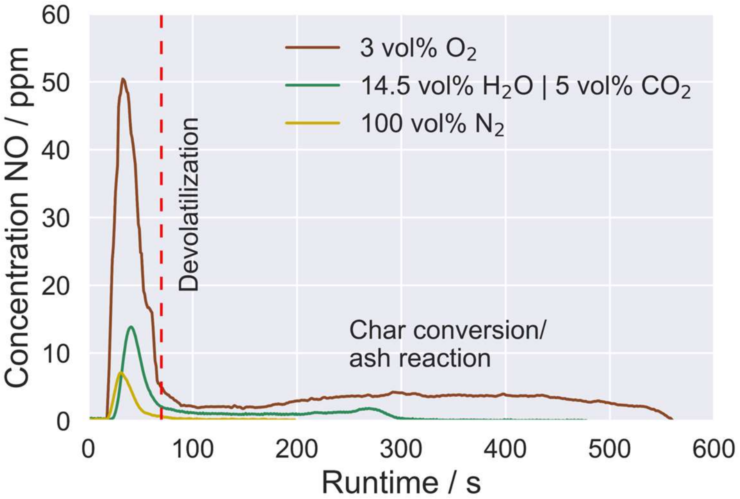

Figure 2: Release of NO during gasification (with H_2O, CO_2, and N_2), combustion (using O_2 and N_2), and devolatilization (under N_2 atmosphere) of raw wheat straw at 950 °C. The dashed line distinguishes between the devolatilization part and the char conversion/ash reaction part.

The diagram in Figure 2 displays curves obtained from both combustion and gasification experiments, which revealed distinct stages of devolatilization and char conversion. The devolatilization experiment performed under 100 vol% N_2 showed no char gasification or ash reaction. It is worth noting that devolatilization exhibits a relatively rapid mass loss rate, while ash/char conversion progresses much slower, as is typical for biomass thermal conversion. Furthermore, the release of NO showed a remarkable decline in an oxygen-poor atmosphere, while an oxygen-rich environment demonstrated a significant peak. The quantity of NO released was assessed through peak integration and categorized into devolatilization and char conversion/ash reaction parts. Specifically, the data was analysed based on the baseline or progress of the NO concentration. In doing so, the integration intervals were specified graphically for both devolatilization and char conversion/ash reaction parts; that is, the char conversion followed immediately after the devolatilization has ended. NO_2 and N_2O were not considered in this work, and the focus was on NO. Among NO_x and N_2O, NO is the dominant species, and NO typically represents the largest fraction released for chopped herbaceous fuels in general [46].

Figure 3 illustrates the correlation of the distribution between volatile-N and char-N, depending on whether the fuel samples were pre-treated before or not. It should be noted that the amount of vol-N in treated biomass is typically lower compared to the untreated source material, as nitrogen was removed during treatment. As for the amount of char-N, it is approximately the same for the raw and pre-treated materials, and the reason lies in stronger bound nitrogen constituents.

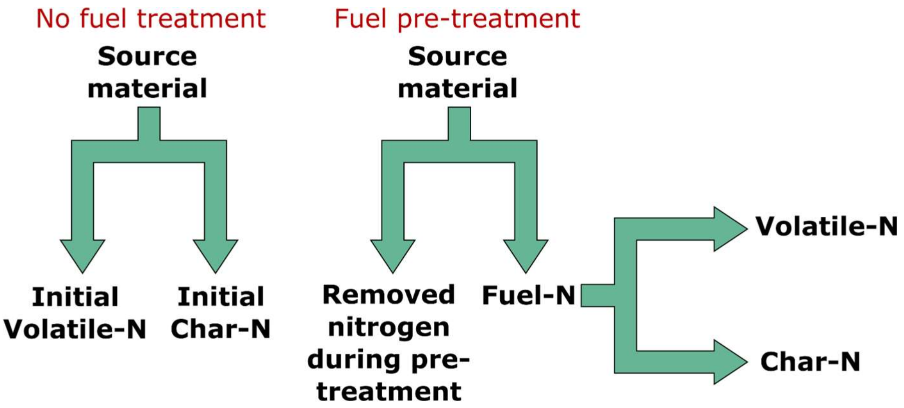

Figure 3: A schematic illustration of the fate of the nitrogen in a fuel. The left sketch depicts the nitrogen distribution if no pre-treatment was applied whereas the right sketch highlights the effect after pre-treatment (torrefaction, water-leaching or a combination of both steps). Modified after Schmid et al. [12].

The fuel-N is represented by the nitrogen content present in the fuel, while the volatile-N and char-N content were determined from the release experiments, as illustrated in Figure 2 (100 vol% N_2). Specifically, the distribution of N in the volatiles and in the char were determined from devolatilization experiments, which were conducted in a pure N_2 atmosphere. The char-N fraction was determined from the remaining N in char, and the vol-N content by the difference between fuel-N and char-N. The removed-N content was not determined experimentally and has been approximated. It was calculated based on the torrefaction grade and/or the residual organic content after pre-treatment.

3. Results and discussion

3.1. Composition of pre-treated fuels

The proximate and ultimate analysis are given in Table 2. Depending on the applied pre-processing method, the amount of ash-forming-matter varies noticeably. Torrefied samples show in general a noticeably higher carbon content in comparison with the source material or water-leached samples. The potassium content in the water-leached sample was reduced by >80%. This means that potassium is mainly bound in the fuel in form of water-soluble salts. The sulfur content also appears to be slightly reduced by washing the fuel. Note that sulfur can only be removed partly due to different solubility of several sulfur compounds, e.g. organic sulfur, alkali sulphates and alkaline earth sulphates. No direct conclusion can be drawn regarding the nitrogen content. However, it is conceivable that torrefaction treatment may have a tendency to increase its content.

Table 2: Ultimate analysis, moisture content and char yield of the untreated and pre-treated fuel samples. The numbers are based on dry matter, while oxygen was calculated by difference.

wt%	**Raw**	**To**	**WL**	**WL-To**	**To-WL**	**To-WL + A**[*]
Moisture	4.54	1.13	4.38	0.24	4.21	4.05
Char	20.6 ± 0.3	29.2 ± 0.6	17.6 ± 3.3	23.8 ± 0.8	24.7 ± 1.1	26.1 ± 0.1
Ash	5.32	7.17	2.47	3.34	3.45	5.45
C	44.1	50.1	44.9	51.2	49.5	48.8
H	5.71	5.35	5.80	5.62	5.48	5.39
N	0.39	0.48	0.28	0.37	0.44	0.43
O	47.0	40.7	47.9	41.2	42.5	42.5
S	0.09	0.17	< 0.10	< 0.10	< 0.10	< 0.10
mg kg^{-1} dry fuel	Ash components (major elements only)					
Cl	3360	424	127	113	298	298
Al	20	20	20	20	61	61
Ca	2010	1747	340	845	2640	10649
Fe	10	7	7	7	76	76
K	13000	17840	2360	3214	6400	6400
Mg	468	716	248	358	588	588
Na	90	90	90	90	200	200
P	220	320	78	96	210	210
Si	7840	10130	7410	10640	10200	10200

[*] Note that the chemical characterization of major ash components of To-WL has been taken into account for the To-WL samples plus Ca-additive. Only the value for Ca was determined on a molar basis, as 2 wt% $CaCO_3$ corresponds to 0.02 mol, which is the equivalent to 0.8 wt% Ca.

Overall, torrefied samples show an increased inorganic content, which is evident in the form of higher ash yield. Comparing the Ca content of the To-WL sample with other pre-treated samples, it appears that the former has a notably higher Ca concentration. This observation fits partially also for other elements, for example potassium. Abelha et al. [47] have shown that the fuel-Ca concentration of wheat straw increased with torrefaction from 2800 mg kg^{-1} (raw material) to 3600 mg kg^{-1} (torrefied material), and the results are in a good accordance with the present ones.

Despite torrefaction treatment, the proportion of potassium in the fuel remains nearly constant and can only be reduced through water-leaching. However, regardless of the pre-treatment method used, the chloride content is significantly reduced. The observed trend clearly indicates a significant difference between the pre-treatment sequences (WL-To and To-WL), despite both samples having a similar ash content with only a 3% variance. It was observed that the proportion of inorganic components was higher in post-washed samples compared to the pre-washed ones. As previously reported in [48], torrefied samples are known to exhibit improved hydrophobic characteristics. The hydrophobic nature of the thermally pre-treated material can potentially hinder the effectiveness of the subsequent leaching treatment. This is likely because the chemical matrix undergoes changes, causing alkali metals to bind differently, possibly in the form of less water-soluble salts, such as sulfates or silicates. Additionally, it is possible that alkali metals may be bound with organic compounds as cations associated with carboxylic acids or inorganic compounds.

3.2. Fuel nitrogen distribution and NO release (from combustion and gasification experiments)

Figure 4 displays the distribution of char-N, volatile-N and removed-N. It can be seen that around 40-60% of the nitrogen is volatile-N, while 20-40% of the nitrogen is char-N. Approximately 10-30% of the N was removed during the pre-treatments, which is consistent with previous research [8,49,50]. Abelha et al. [47] reported a decrease in nitrogen content by pre-washing miscanthus and roadside grass, suggesting that some of the fuel-N must be present in water-soluble forms, such as ammonium salts or amines, in the feedstock. These results are consistent with other studies found in the literature, which have also observed a decrease in nitrogen content during water-leaching [51,52].

In this study, the removed N-content was approximated and calculated based on the torrefaction grade (T_G = 27.8%), and/or the residual organic content after treatment. The organic fraction of the treated samples was determined based on their ash content. Based on Table 2, raw wheat straw was found to have an ash content of 5.32 wt%. Therefore, it can be expected that the residual organic content is 94.67 wt%. An ash content of 2.47 wt% was determined for the water-leached sample, resulting in an organic matter content of 97.53 wt%. By calculating the ratio between the raw and washed sample, a factor of 0.97 was obtained. For instance, multiplying this factor with the N-fuel content of the washed sample (0.28 wt%) equals 0.27 wt%. The raw fuel had a N-content of 0.39 wt%, indicating that about 0.12 wt% of nitrogen was removed. The torrefaction degree was taken into account for calculating the removed nitrogen content in both washed and torrefied samples.

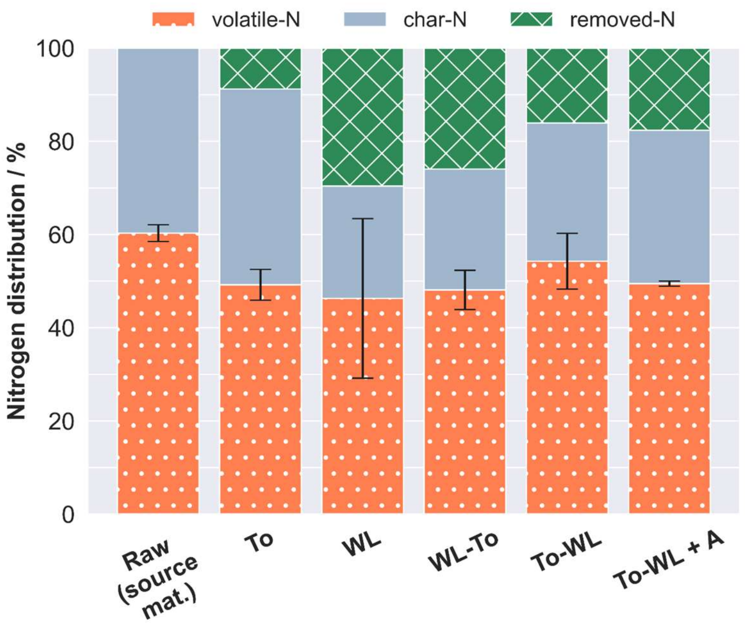

Figure 4: Distribution of volatile-N, char-N and removed-N. The approximated amount of removed-N was lost during pre-treatment and calculated based on the fuel-N content in raw wheat straw (source material). Note that the error bars refer to char-N.

The initial ratio of volatile-N/char-N for the raw material was 60/40, while for the torrefied sample, it was 49/40. The volatile-N/char-N ratio remained almost constant for the water-leached, pre-washed, and post-washed samples. The calculated approximation showed that approximately 10% of the initial nitrogen was removed during the torrefaction treatment, while roughly 30% was removed during the water-leaching treatment. A schematic depiction of the distribution correlation between vol-N and char-N is shown in Figure 3 of the Materials and Methods section.

Figure 5 displays the total amounts of NO released during the combustion and gasification experiments. For the sake of clarity, the results were also presented in the form of numbers (see supplementary information). As shown, the pre-treated samples generally produced lower NO emissions than the raw material, except for torrefied fuels which had significantly higher emissions. Combustion (3 vol% O_2) of the raw material resulted in about 790 µg NO per gram fuel, while the torrefied fuel emitted approximately 960 µg. However, it should be noted that the torrefied straw had a higher N-content than the original straw (0.48 wt% vs. 0.39 wt%). In contrast, the water-leached samples showed a significant decrease in NO emissions (approx. 480 µg NO/g fuel), indicating a reduction of over 40%. During gasification, the NO emissions were expectedly lower than during combustion due to the lack of O_2. Furthermore, NO emissions were further suppressed when H_2O was added to the gasification gas.

It is noticeably that the water-leached samples showed the lowest NO release, and these observations are in accordance with the distribution of removed-N in Figure 4, where it was shown that washing removed approximately 30% of fuel-N. Compared to the WL-To samples, the To-WL samples exhibit slightly increased NO emissions under all reaction conditions, including combustion and gasification-like environments. These observations, in addition to the chemical analyses, provide further evidence that the pre-treatment sequence may influence the release behavior of inorganic species.

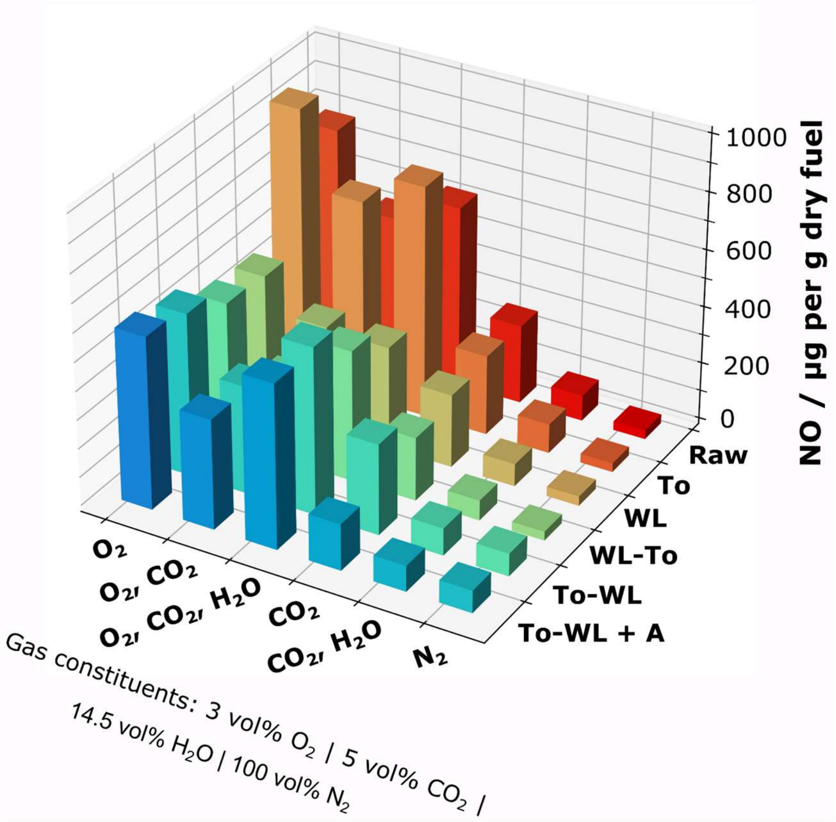

Figure 5: NO emissions in μg g^{-1} dry fuel under different atmospheric conditions at 950 °C. The balancing gas was N_2. Results are also presented in the form of numbers (see supplementary information).

It is noteworthy that the To-WL sample with $CaCO_3$ additive exhibits a slight increase in NO emissions during combustion (3 vol% O_2) compared to same sample without the additive. Similar observations have been reported for coal combustion in previous studies, where limestone was found to increase NO emission [53,54]. In the case of petroleum coke combustion, Liu et al. [55] have investigated the impact of limestone on NO emissions, which is influenced by the contact between gas-solid components. If there was a sufficient contact between the calcium compounds and the gaseous products, NO emissions might decrease [55]. However, the reaction mechanism is not yet fully understood.

Note that the amount of emitted NO does not directly correspond to the N-content in the parent fuel. Although the N-content in the To-WL material is higher than in the raw material itself, significantly less nitrogen is released under combustion or gasification-like conditions. Ren et al. [35] reported in a previous study that torrefied samples generally exhibit varying NO emissions, depending on the biomass types. A recent study in [12] underlined the fact that the overall nitrogen content in the parent fuel is an insufficient indicator for predicting NO_x formation.

The conversion of fuel-N to NO is additionally illustrated in Figure 6, where the devolatilization and char conversion stages are separated into their respective conversion components – volatile-N to NO and char-N to NO. In a combustion environment (3 vol% O_2), the fuel-N conversion to NO is unsurprisingly higher than in a gasification-like atmosphere (14.5 vol% H_2O and 5 vol% CO_2). This becomes evident when the release activity of the source material is compared under both oxidizing and reducing atmospheres. Under 3 vol% O_2, 95% of the fuel-N was converted to NO, whereas under 14.5 vol% H_2O and 5 % CO_2, only 12% of the fuel-N was converted to NO. In general, the combined pre-processing has a suppressing effect on the fuel-N to NO conversion. For the torrefied-water-leached material, approximately 60% of the fuel-N resulted in NO formation (in 3 vol% O_2), indicating a 35% decrease in comparison to the raw sample.

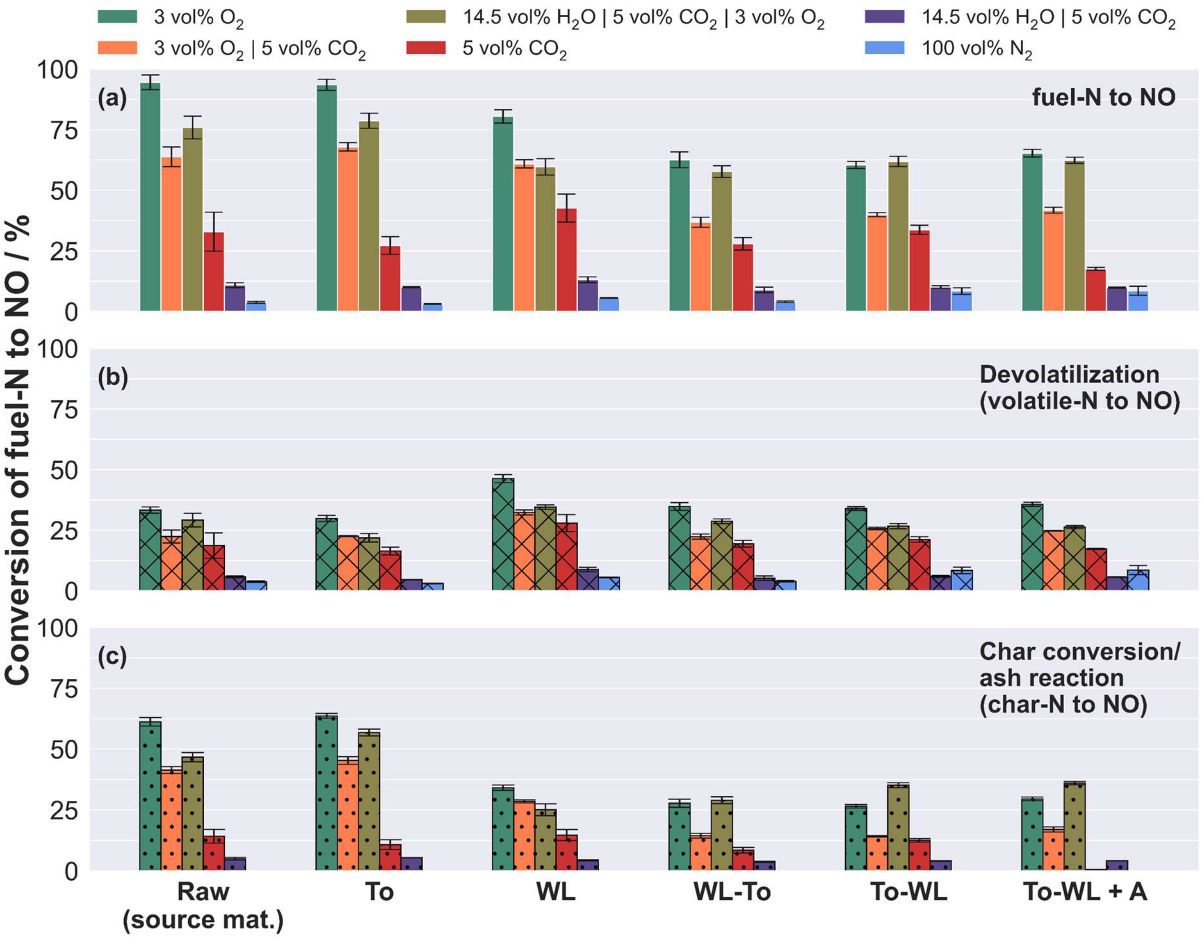

Figure 6: Conversion of fuel-N to NO at 950 °C: the upper part (a) shows the conversion of fuel-N to NO, the middle part (b) volatile-N to NO (devolatilization) and the lower part (c) char-N to NO (char conversion).

The water-leached samples demonstrated increased conversions of volatile-N to NO in comparison to the raw or torrefied material. However, during char conversion, all pre-treated samples, except for the torrefied sample, produced lower NO emissions. Approximately 62% of the char-N formed NO during char conversion for both the raw and torrefied samples, while 26% to 35% was formed for the samples that were washed prior to or subsequent to thermal treatment. This suggests that the N-content is not a crucial factor in the conversion of volatile-N or char-N to NO, as stated earlier. For combustion conditions, it can be concluded that CO_2 appears to decrease NO emissions, while H_2O appears to increase them. These effects seem to hold true for CO_2 in both devolatilization and char conversion/ash reaction steps, but for H_2O, this is primarily observed during char burning. In gasification, H_2O appears to decrease the formation of NO, and this holds true for both conversion steps.

Earlier studies [12,43] reported on the effect of pre-processing on the conversion of char-N to NO. The results showed that for biomasses with low nitrogen contents, the conversion of char-N to NO for demineralized samples exhibited the highest conversion rates compared to the untreated materials. Interestingly, for biomasses with high nitrogen contents, an opposite trend was observed. The observations made in this work do not align with those of [12,43]. While the investigated straw samples displayed a relatively low nitrogen content, the conversion of char-N was observed to be higher in the untreated materials compared to the water-leached or water-leached and thermally treated ones. It seems difficult to explain these discrepancies, and the cause of this phenomenon remains unclear. The presence of catalytic elements (ash components) is lower in water-leached samples, therefore, assumed catalytic effects are expected to be decreased during the char oxidation state. One possibility could be attributed to chemical kinetics, e.g. more char surface could be available for the reduction reaction in the absence of inorganic elements [43]. It was observed that washed samples, or samples that were washed and thermally treated, typically swelled during devolatilization. This consequently increased the sample surface.

3.3. Formation of NO, NH_3 and HCN during devolatilization

The NO_x precursors NH_3 and HCN are released during devolatilization [8,13]. The high temperature chemistry of NH_3, HCN and other nitrogen-containing species has been investigated in numerous studies (see e.g. [15]). HCN is the predominant cyanide species and it can be further converted to NH_3 [34]. NH_3 and HCN can react to imidogen (NH), a highly reactive radical. The reaction mechanism proceeds through intermediate steps that vary depending on combustion parameters like stoichiometry, gas temperature, and so on [8,56]. The nitrogen chemistry is predominantly governed by NH_3 instead of HCN. Therefore, controlling the selectivity for NO and N_2 formation at the rich-lean transition in the staged combustion process is achieved [34]. The minimum in NO is due to competition between the reduction of NO by NH_3 and HCN and the oxidation of NH_3 or HCN [57]. NH_3, in particular, can significantly impact the gas phase depending on its composition. However, its interaction with hydrocarbon oxidation chemistry, especially under reduction conditions, is complex as seen in [34].

The rates of conversion of volatile-N to NO, NH_3, and HCN during devolatilization at 950 °C are shown in Figure 7.

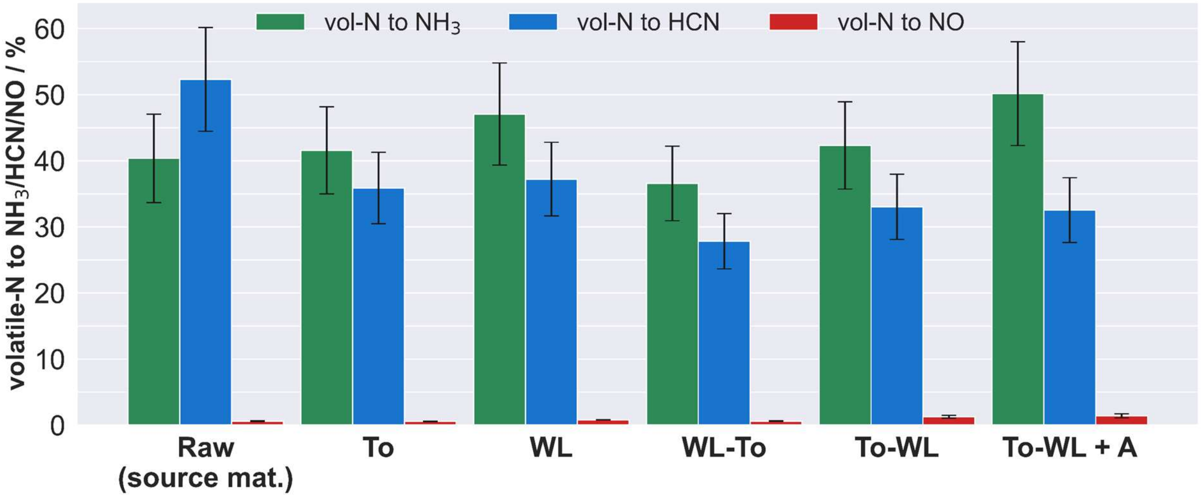

Figure 7: Conversion of volatile-N to NO, NH_3 and HCN during devolatilization in 100% N_2 at 950 °C.

For the pre-treated samples, except for WL-To, the conversion of volatile-N to ammonia is slightly higher than for the untreated sample. Furthermore, a notable increase in NH_3 formation is observed between the postwashed sample and the sample postwashed and blended with 2 wt% $CaCO_3$. Similar observations were made in a recent study published by Schmid et al. [12], who used the same reactor system and demonstrated that biomass with a higher calcium and lower potassium content produced more NH_3. The results in Figure 10 indicate that ash-forming elements, such as calcium or potassium might impact on the formation of NH_3 [16,38–40]. In contrast, no trend can be observed for the activity of formed HCN. Interestingly, the conversion of vol-N to HCN appears to be dominant for the raw material, whereas for the torrefied material most of the vol-N is converted into NH_3. It can be assumed that there are various reasons influencing the conversion process such as different intrinsic properties or N-functionalities, as reported in [14]. It seems clear that N-functionalities may impact on the fate of N during devolatilization, as the structure and complexity of biomass makes further interpretation difficult. One possible explanation that is also supported by the results from Figure 10 is the influence of ash-forming matter in the fuel. Calcium seems to support the NH_3 formation. This can be specifically observed when comparing the To-WL samples with the same sample with $CaCO_3$ addition, as depicted in Figure 7.

The impact of the precursors is further clarified in Figure 8, where the production of NO, under different atmospheric conditions (either oxidizing or reducing), is presented as a function of the proportion of precursors generated during devolatilization experiments (100 vol% N_2). It can be seen that there is a minor correlation between the release of NO and the precursors HCN+NH_3, and it seems that this connection slightly increased with a rise in nitrogen concentration in the precursors but only under combustion conditions. Furthermore, the results demonstrate a modest trend implying that demineralized samples (those that were water-leached or water-leached and torrefied) emit a lower quantity of NO compared to samples that were simply torrefied or those that underwent torrefaction prior to water-leaching. The trend in Figure 8 nonetheless suggests that the NO emission is primarily less dependent on the nitrogen concentration in the precursors, but instead much more dependent on the gas atmosphere. Note that there are various factors that may impact the formation of NO during biomass combustion and gasification, such as fuel particle size, operating temperature, and the residence time or the time for which the fuel is exposed to a high temperature zone. However, these parameters were kept constant throughout the study and can be therefore disregarded. In general, it can be concluded that the results agree well with the NO emissions shown in the previous 3D bar chart (Figure 5), where the gas composition was found to play a crucial role in NO release. Combustion conditions (e.g., O_2) resulted in the highest amount of NO emissions, while the lowest quantity was observed under gasification-like conditions (e.g., H_2O and CO_2).

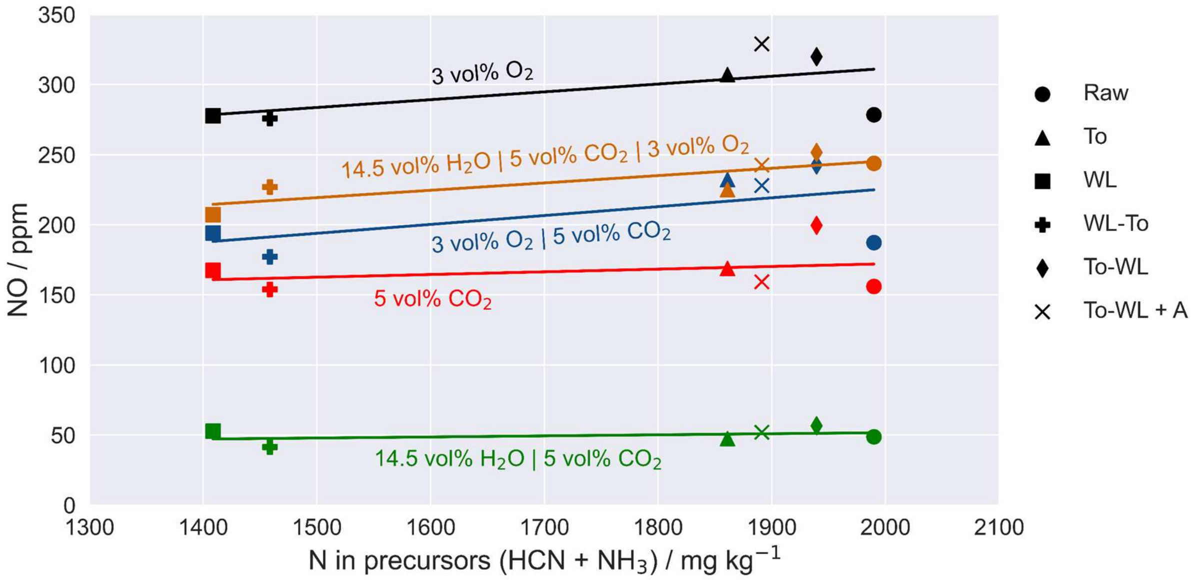

Figure 8: Correlation between NO release in various atmospheres and NH_3/HCN formation from devolatilization experiments (100 vol% N_2) at 950 °C.

Recent studies [12,13] have indicated that increasing the fuel-N content while reducing the H/N ratio leads to a higher HCN/NH_3 ratio, which is related to the formation mechanism of NH_3 and HCN. The presence of hydrogen may convert HCN into NH_3 [12]. Therefore, Figure 9 shows the experimentally determined molar HCN/NH_3 ratio in pre-treated samples as a function of the fuel-N content or molar H/N ratio. As the nitrogen content in the examined samples was relatively low, no definite conclusions can be drawn.

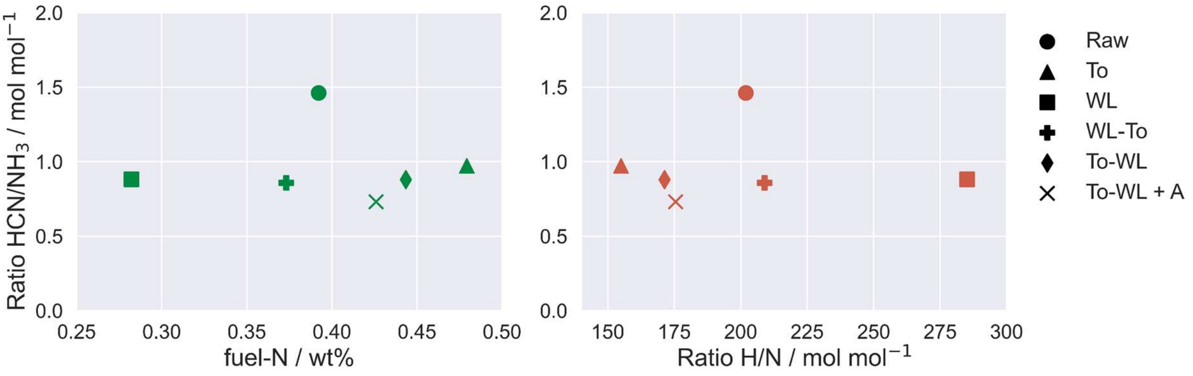

Figure 9: Molar HCN/NH_3 ratio versus fuel-N (left) and molar H/N ratio (right).

Several studies [16,38–40] investigated how pre-treating biomass, e.g., by demineralization, influences the formation chemistry of NO, NH_3, and HCN. These studies suggest that ash-forming elements, such as calcium or potassium, may promote catalytic effects on the formation of NH_3 and HCN during devolatilization.

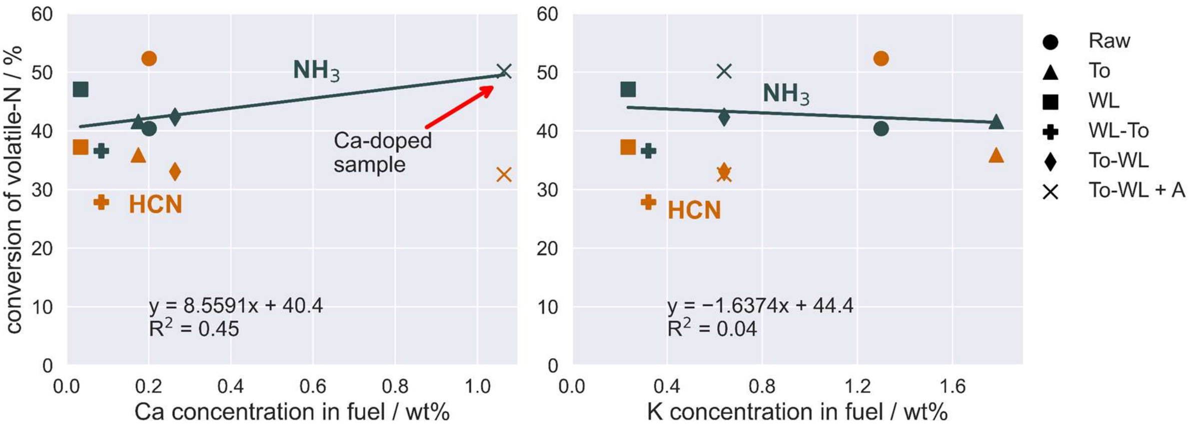

Figure 10: Conversion of volatile-N to NH_3 and HCN as a function of Ca (left) and K (right) content in the pre-treated wheat straw samples. Blue color represents NH_3 and brown represents HCN. The arrow on the left-hand side of the diagram indicates the Ca-doped sample.

There is no clear trend observed for HCN formation when comparing changes in calcium or potassium concentration. However, for NH_3, the results suggest that more ammonia was formed in the samples, containing higher calcium content and lower potassium content. In an earlier study conducted by Schmid et al. [12], the same trends were observed for the conversion of volatile-N to NH_3 and HCN in both pre-treated bark and wheat straw. Yi et al. [40] found that during pyrolysis of proteins and amino acids in herbaceous feedstocks, Ca enhanced the formation of NH_3 and reduced the formation of HCN. The nitrogen chemistry during char oxidation could also be influenced by the ash-forming matter. Winter et al. [58] reported that during char conversion, char-N reacts with oxygen to mainly form NO, which can be heterogeneously reduced by char-C to nitrogen. Both calcium and potassium in the char are believed to influence the conversion of char-N by catalysing the reduction reaction between NO and char [30]. In a recent study, demineralised biomass exhibited noticeably more NO release compared to raw biomass fuels [43].

4. Conclusions

The work investigated the influence of various fuel pre-treatments on nitrogen emissions during combustion and gasification of herbaceous wheat straw feedstock. The aim was to understand the fate of fuel-bound nitrogen and the impact of single and combined upgrading methods. A detailed comparison of these methods helped gain knowledge and clarify their impact on the release of N-species.

The results showed that the water-leached samples had the lowest NO emissions based on fuel mass, while the torrefied materials had the highest emissions. These observations can mainly be attributed to the correlation between NO emission and the amount of fuel-N, as the water-leached sample showed the lowest fuel-N content while the thermally treated sample showed the highest fuel-N content. The sequence of pre-treatment had an impact on the NO emissions during their combination. The NO emissions were higher when the torrefaction was done before washing, whereas lower emissions were observed when the samples were first washed followed by torrefaction. This implies that the pre-treatment sequence plays a role in influencing NO emissions.

Under oxidizing conditions, the formation of NO was found to be correlated to the production of NO precursors such as NH_3 and HCN. However, this particular correlation was not observed under gasification conditions, indicating that the NO released during gasification mainly originates directly from the fuel. The analysis clearly demonstrates that the atmosphere has a significant higher influence on the NO formation than the quantity of NO precursors.

It is worth noting that the NO emissions in a gasification or combustion environment are not directly proportional to the N-content in fuel. The findings of this study suggest that various factors influence NO emissions, including the contents of ash-forming elements (having catalytic effects) or the surrounding gas atmosphere. Additionally, biomass upgrading supports the hypothesis that NO emissions depend on how nitrogen is bound to the biofuel [8], since pre-processing modifies the chemical composition of the feedstock. Finally, the high process temperature plays a significant role;

for instance, the high temperature of combustion promotes the oxidation of nitrogen compounds and molecular nitrogen (which is present in the environment and strongly depends on the surrounding gas atmosphere) to nitric oxides (thermal NO_x). As discussed in the introduction section of this study, significant levels of NO_x are usually formed at temperatures above 1300 °C under oxidizing conditions, and the levels increase exponentially as the temperature rises. Hence, in this research, thermal NO_x can be disregarded since it is not pertinent to the investigations at 950 °C.

In general, pre-treated samples demonstrated higher conversion rates of volatile-N to NH_3 compared to the source material. However, no significant trend was observed for HCN formation. The highest level of NH_3 production occurred in the To-WL samples doped with $CaCO_3$. Calcium enhanced the conversion of volatile-N to ammonia, whereas potassium tended to reduce its formation. The NH_3 formation during devolatilization was inherently linked to the Ca- or K-content present in the biofuel. There is evidence that characteristic catalytic effects are produced by the species mentioned earlier, which influences nitrogen chemistry through the by ash-forming matter.

Concerning the char-N to NO conversion, it was discovered that the NO conversion rate was higher for the source or torrefied material than for the water-leached samples. Additionally, the NO conversion rate during char conversion/ash reaction was higher for the torrefied samples compared to the raw material itself, regardless of the reaction conditions (combustion or gasification-like environment). Washing the samples before or after thermal treatment resulted in relatively constant NO conversion rates. Still, minor increases in NO conversions rates were observed for the To-WL samples when comparing them to the WL-To samples. In a recent publication [42], we reported that torrefaction could improve the hydrophobic characteristics of herbaceous feedstocks. The hydrophobic nature of the thermally pre-treated material may hinder subsequent leaching treatment. This means the chemical matrix changes, and alkali metals may be differently bound in the form of less water-soluble salts, such as sulfates or silicates. The sequence of treatments determines the balance between the inorganic components, which impacts ash-related issues. However, based on the results, it seems that pre- or postwashing of torrefied materials does not affect nitrogen chemistry at all.

In summary, it can be concluded that the applied fuel pre-treatment methods, along with blending with $CaCO_3$, influenced the emission of N-related pollutants. Further investigations on different biomass fuels are needed in order to increase the range of results for adequate conclusions, and more work needs to be done to quantify the effects of operational parameters, such as the surrounding gas atmosphere, process temperature and equivalence ratio on fuel-N evolution during combustion and gasification. Moreover, results of this work have exhibited that N-conversion during devolatilization shows obvious discrepancies, and complex constitution of biomass or different intrinsic properties of

N-functionalities hinder clear mechanistic insights. Therefore, more studies are necessary to assess the origin of NH_3 and HCN.

CEediT authorship contribution statement

Florian Lebendig: Conceptualization, Methodology, Investigation, Writing - original draft. **Daniel Schmid:** Conceptualization, Methodology, Investigation, Writing - review & editing, Supervision. **Oskar Karlström:** Conceptualization, Writing - review & editing, Supervision. **Patrik Yrjas:** Writing - review & editing, Supervision. **Michael Müller:** Writing - review & editing, Supervision.

Conflicts of Interests

The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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