High temperature volatile yield and nitrogen partitioning during pyrolysis of coal and biomass fuels

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**Abstract**

Nitrogen oxides (NOx) are atmospheric pollutants specifically targeted by legislation which imposes limits on emissions from large scale plant. During combustion, part of the Nitrogen fuel will be released as a component of the volatile matter compounds and as volatile nitrogen, while part will remain in the char. Thus, the fate of volatile-N and char-N becomes crucial for the formation of NOx and, consequently, for determining the concentrations of NO in solid fuels combustion systems. In pulverized fuel combustion, major routes for conversion of the volatile-N are either NO or N2, while char-N reacts through a set of heterogeneous reactions as the char is oxidized. Measuring high temperature char nitrogen content of the fuels directly reduces the likely uncertainty in NOx emissions from solid fuels on modern power stations using deep furnace air staging High temperature volatile-N and char-N partitioning is investigated by pyrolyzing fuels in a high temperature (1600°C) wire mesh apparatus (HTWM) and analyzing the resulting char. White wood biomass, olive waste, torrefied wood, two bituminous coals and one anthracite coal were used on this study. The volatile yield at high temperatures has been obtained for each sample. The fate of nitrogen released during the pyrolysis as volatile matter and the nitrogen retained in the char has been evaluated for different biomass samples. The nitrogen in the char was measured using a total nitrogen analyzer. Results show a large change in on the volatile yield compared with proximate analysis values for both coals. Only moderate change was observed on the volatile yield for both of the woody biomass that already have high values on proximate analysis, and just a slight increase was obtained on the volatile yield for the olive waste. Differences were found on the fate of nitrogen retained in the char that would lead to NOx formation. The biomass samples release most of their fuel-nitrogen as volatile (between 80-95%) while on the coals the volatile nitrogen is wide more variable depending on the coal sample.

Keywords: coal, biomass, pyrolysis, NOx, Nitrogen partitioning

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**Highlights**

* Chars were obtained from fast pyrolysis to 1600 ºC in a high temperature wire mesh reactor.
* Volatile yield for different coal and biomass fuels was calculated.
* Nitrogen partitioning for different coal and biomass fuels was obtained.

1. **Introduction**

Nitrogen oxide is an atmospheric pollutant known to cause acid rain, smog and respiratory diseases. It is specifically targeted by legislation which imposes limits on emissions from large scale plant [1]. Flue gas denitrification technologies lower the NOx concentration in the flue gas through reduction reactions to N2. These post-combustion control systems are referred to as selective catalytic reduction (SCR) and selective non catalytic reduction (SNCR).  In either technology, NOx is reduced to nitrogen (N2) and water (H2O) through a series of reactions with a reagent (or reagents) injected into the flue gas. The most common reagents used in commercial applications are ammonia and urea for both SCR and SNCR systems [2]. Although these are efficient technologies, the auxiliary systems add costs to the plant both on the capital expenditure and operation and maintenance cost.

There are three different mechanisms for NOx formation during combustion: thermal NOx, prompt NOx, and fuel NOx. Fuel NOx is formed by the oxidation of nitrogen compounds contained in the fuel. Thermal NOx is formed by high-temperature reaction of nitrogen with oxygen This is generally the predominant mechanism in large scale combustion processes. Prompt NOx is formed by the fast reaction between nitrogen, oxygen, and hydrocarbon radicals. Prompt NOx is formed under fuel-rich conditions but is generally much less significant compared to thermal NOx formation in higher temperature combustion processes. Fuel NOx arises directly from the nitrogen in the fuel and is formed in complex chemistry in both volatile and char combustion steps. Strategies to minimize NOx emissions include actions such as: burning fuel with lower nitrogen in its composition; adjustment of the furnace combustion air configuration and; flue gas treatment.

The overall reaction from fuel nitrogen to NO or N2 is influenced by the reaction conditions: the temperature; the concentration of reducing and oxidizing agents; the flame turbulence and; the residence time in the different combustion zones. Pulverized fuel (p.f.) systems can operate with flame temperatures over 1500°C. Where thermal formation of NOx becomes significant. Other technologies like fluidised-bed systems are found to have lower temperatures in the furnace, therefore limiting thermal NOx formation, although N2O emissions can be an issue. Techniques to minimize the NOx production in p.f. boilers have been developed such as ‘Low NOx‘ burners that reduce the peak temperature of the flame. Other established methods of controlling the flame peak temperatures include secondary and tertiary air mixing. Where, again, reduced flame temperature leads to less NOx formation [3]. This effective technique for reducing thermal NOx, is called air-stage combustion.

Nitrogen content in the fuel also has a large influence on NOx formation and is therefore routinely monitored by ultimate analysis of the fuel. The NOx emissions on coal fired power stations can be predicted from proximate and ultimate analysis under certain premises with an accuracy of 20%. Many biomass fuels contain organic molecular bound nitrogen in the form of aminoacids and proteins [4] . In high temperature combustion, this nitrogen forms precursor compounds for the formation of nitrogen oxide. Some biomass fuels, especially those from agricultural sources, may contain significant amounts of organically bound nitrogen. Biomass nitrogen content could be very variable among samples and even during the session [5]. The variability on the fuel composition affects the combustion properties, particularly the nitrogen content and forms in the fuel affects the fate of volatile nitrogen released and the nitrogen species formed [4]. Darvell et al. [6] analyzed common biomass fuels imported to UK power stations, and obtained volatile-N between 79-91 %. The pyrolysis conditions, such as temperature or heating rate, also affect the volatile yield and the species formed.

McNamee et al. [7] found that torrefaction can affect the nitrogen partitioning; lowering the N content in the fuel and improving the nitrogen release as volatile-N.

During pyrolysis of the fuels part of the nitrogen is released as part of the volatile matter compounds, while part remain in the char. Nitrogen is released as HCN, NH-compounds (including NH3), NO and N2 [6]. The volatile-N is transformed mainly into either NO or N2, while char-N reacts through a set of heterogeneous reactions as the char is oxidized; oxidation of char –N to NO and reduction of NO on the char surface become competing reactions that impact on NOx emissions on the one hand and carbon burnout on the other.

Fuel nitrogen is normally described to be converted into ammonia (NH3) and hydrogen cyanide (HCN) as intermediate compounds during combustion [8,9]. Biomass volatile-N is predominantly liberated as NH3, which may be oxidised to NO but also acts as a reducing agent in further reactions with NO to form N2 [10]. On the other hand, coals release less volatiles and the fuel-N is mainly evolved as HCN, which has a lower potential to reduce NO to N2. Under fuel-rich condition, the presence of large amounts of hydrocarbons from fuel pyrolysis, unburnt char and CO favoured the reduction of NO to HCN, NH3 and molecular nitrogen N2. Thus, the fate of volatile-N and char-N becomes crucial for the formation of NOx and, consequently, for determining the concentrations of NO in solid fuels combustion systems.

Cofiring biomass with coal has been reported to be a good way to reduce NOx emissions (compared to 100% coal) not only due to the lower nitrogen content of the biomass materials but also synergetic effects on the combustion that reduce the formation of NOx [11]. Riaza et al.[12] postulate that increase proportion of hydrocarbons from volatiles coming from the biomass may have a reducing effect within the flame. Besides the differences in nitrogen content, NOx precursors and species formed, most of the biomass is released as volatiles, creating a greater reducing environment on the flame development zone, even though there is a lot of oxygen in the volatiles.

Munir et al [13] compared the effects of air-staging and biomass addition showing the relationship between the over-firing air (OFA) injection location, stoichiometric ratio and NO reduction efficiency in a drop tube reactor.  It was found that a decrease in primary zone stoichiometry and an increase in residence time, by varying OFA port location in the primary zone, both have a positive effect on NO reduction for coal and coal–biomass blends co-firing.

Wire mesh reactors (WMR) have been used in some studies to obtain high temperature/high heating rate chars which are analysed for morphology, reactivity, and other combustion characteristics [14-18]. WMR is able to achieve conditions that resemble those of industrial boilers, namely high heating rates of 103 -104 ºC s-1, temperatures up to 1600 ºC, and on demand residence times. Although DTF can achieve higher heating rates in the order of 104 - 105 ºC s-1 which are closer to those found in industrial boilers, WMR has the advantage of fast, easy, and flexible operation, i.e. operating condition parameters such as temperature, heating rate, pyrolyzing atmosphere, and residence time can be changed separately. The volatile yield depends mainly on operating parameters such as temperature, heating rate, and residence time [19-24].

The heating rate during pyrolysis has an influence on the char structure and morphology. During pyrolysis of either coal or biomass, an unstable intermediate phase - metaplast, is formed [25], which determines the subsequent softening of the char particle. At low heating rates, cross-linking typically occurs before bridge-breaking which reduces the plasticization of the char [19]. However, at high heating rates the plasticization is enhanced as bridge-breaking takes place before cross-linking [19], and higher char fluidity, extensive melting and swelling could be achieved.

Previous works done by Man et al [14] tested series of world-traded coal samples using a high temperature wire mesh apparatus (HTWM) in order to assess the relationship between high temperature (1600°C) char nitrogen content and NOx formation in Power Station using deep furnace air staging. These studies confirmed a linear relationship between high temperature char nitrogen and NOx formation. These results imply that high temperature char nitrogen content is the main factor limiting NOx emissions with deep air-staged combustion. The experiments also showed the high temperature volatile yield of the fuels to be much higher than that obtained in standard procedures.

Understanding of the fate of fuel bound nitrogen is important in the control of the NOx produced at different stages of combustion. The partitioning of fuel bound nitrogen between the volatile flame and the char particle is key to understanding and estimating the NOx emissions during deep air-staged large scale combustion. Data for biomass nitrogen content in char obtained at high temperature conditions is rarely found in the literature, often because the N-content is low and close to or below the detection limit of standared CHN analysers.

Here, experiments on a HTWM have been undertaken using various biomass and coals, with the objective of evaluating the volatile yield at high temperatures (1600 ºC) and obtaining high temperature char for nitrogen content analysis. A N-analyser with chemiluminiscence detector gives improved accuracy and also provides further detail of volatile-N and char-N contents.

1. **Materials and methodology**
   1. **Fuel samples used**

A series of experiments have been made with three different biomass and three different coal samples. The biomass sample used were white wood pellet (WP), olive waste (OW), and steam torrefied wood pellet (BP). Coal A was originally from El Cerrejon, Colombia; Coal B was originally from India and Coal C is an Anthracite from Vietnam. Each fuel was characterized in terms of chemical composition by proximate analysis [26-28], ultimate analysis [29] according to standard testing methods, and gross calorific value [30], results are presented in Table 1.

WP has the typical composition of a commercial wood pellet widely used for domestic and industrial heating, with very low ash content, high volatile matter content and a calorific value lower than the coal. Both woody biomass samples, BP and WP, have low amount of nitrogen in their elemental analysis. However OW has a notable nitrogen content (1.6% daf) that is higher than coal C and equal to coal B nitrogen elemental composition.

**Table 1. Proximate and ultimate analysis of the samples used.**

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | **OW** | **BP** | **WP** | **Coal A** | **Coal B** | **Coal C** | basis | units |
| **moisture content** | 5.9 | 7.2 | 6.7 | 5.5 | 7.3 | 7.7 | as received | %wt |
| **ash content** | 7.6 | 4.2 | 0.8 | 1.5 | 34.1 | 34.6 | dry | %wt |
| **volatile content** | 80.1 | 79.4 | 84.3 | 40.1 | 41.6 | 9.6 | daf | %wt |
| **fixed carbon** | 19.9 | 20.6 | 15.7 | 59.9 | 58.4 | 90.4 | daf | %wt |
| **GCV (dry)** | 20.1 | 20 | 20.8 | 32.7 | - | - | dry | MJ.kg-1 |
| **C** | 52.8 | 52.7 | 52.3 | 73 | 74.1 | 91.1 | daf | %wt |
| **H** | 6.5 | 5.8 | 6.8 | 5.2 | 4.7 | 3.2 | daf | %wt |
| **O** | 39.1 | 41.2 | 40.7 | 19.6 | 19.6 | 3.6 | daf | %wt |
| **N** | 1.6 | 0.20 | 0.16 | 2.2 | 1.6 | 1.4 | daf | %wt |

Each sample was milled, dried and sieved to different ranges of sizes. Coals were sieved down to a size range of 125-150 µm as used in the previous study by Man et al. [14]. The particle size ranges used for the biomass were 300-500 μm, 500-710 μm and 1120-1400 μm. These sizes were selected to be high enough to prevent the pyrolyzed particles from falling through the wire mesh aperture (60 µm), low enough to enable the assumption of uniform particle temperature, and representative of the largest size fraction that would be entering a pulverized fuel boiler. Samples are dried in an oven at 115 ºC for 2 hours to remove any moisture before pyrolysis experiments in the wire mesh reactor.

* 1. **Experimental device**

A new HTWM system has been developed at the University of Edinburgh to obtain high temperature char and evaluate volatile yield at high temperature. This reactor was based on the WMR used by Man et al. [14], and is shown schematically in Figure 1. The reactor consisted of a wire mesh to place and heat the sample, insulated electrodes to supply high current, a thermocouple to measure the mesh temperature, and a glass chamber to control the pyrolysis atmosphere.

The wire mesh is made of molybdenum to withstand a temperature of 1600 ºC under non-oxidizing conditions. The mesh has an aperture of 60 µm and wire diameter of 35 µm, and an area of 80x40 mm. The two wire meshes were placed parallel and horizontally, clamped and connected to two copper terminals in both extremes.

The high temperature/high heating rate conditions in the reactor were attained using a high current/low voltage power source, and controlled by means of a program developed in LabVIEW to obtain reproducible results. The heating control method was based upon knowing the anticipated power demanded to reach a specified temperature [31]. Accordingly, the output current was limited to enable an operating mesh temperature of 1600 ºC, and heating rate estimated to be above 103 ºC s-1. The temperature was measured with an unsheathed 50 µm diameter R-Type thermocouple placed on direct contact with the bottom mesh, and was logged using the LabVIEW program. The residence time is defined from the instant when the program applies the current to heat the mesh until it stops heating. The estimated heating time to reach maximum temperature is 1 second.

Pyrolysis experiments in the wire mesh reactor were performed by the following steps:

1) a thin layer of evenly spread fuel sample was weighted and placed between two meshes;

2) the meshes with fuel sample were clamped to the copper terminals;

3) the reactor was sealed within a glass chamber;

4) the chamber was evacuated to remove air and then filled with helium gas up to ambient pressure;

5) the power source was turned on to heat the mesh to the specified temperature and to keep the temperature constant for a specified time;

6) when the pyrolysis was completed, the chamber was cooled under inert atmosphere and char sample was collected, weighted and stored for further analysis.

Experiments on a HTWM have been undertaken with varying parameters of particle size, residence time and maximum temperature.

**Figure 1. High temperature wire mesh reactor (**HTWM**) schematic representation.**

The mass loss due to devolatilization was evaluated on every run. The volatile yield on each experiment was calculated based on the difference between the weight of the sample placed on the wire mesh and the char collected.

Nitrogen content on the char was under detection limit (<0.3) for most HCN elemental analyzers. A [Total Nitrogen Analyser (Analytik Jena Multi 5000](https://apps.engineering.leeds.ac.uk/booked/engineering/Web/reservation.php?rid=116&sid=6&rd=2018-02-06)) capable of measuring nitrogen content to 0.002% (by weight) was therefore necessary. This analyser has enabled confident assessment of N-partitioning between volatile and char under different conditions with a precision of 0.002% (0.02mg per gram).

1. **Results and discussion**
   1. **High temperature volatile yield**

The volatile matter content of the biomass samples using the standard procedures for proximate analysis is typically high. Higher temperatures facilitate the pyrolysis to develop further, and the residence time is a critical parameter for the biomass to release the entire potential volatile yield. Temperature and residence time are this key parameters for pyrolysis, and therefore the volatile yield obtained. Different values for residence time were used in a series of experiments with WP biomass at 1600 ºC. The repetition of the experiments showed an average standard deviation of 4.4% on the volatile yield. Results are represented in Figure 2.

**Figure 2. High temperature volatile yield obtained at different residence time for WP**

Volatile yield increases as the residence time increases up to 4 seconds. After that time the sample becomes more stable and the volatile yield does not increase much more. A similar plateau was observed by Farrow et al [22] when doing pyrolysis of biomass in a DTF in N2 at temperatures up to 1450 ºC, although the same conditions with CO2 atmosphere reduced the char to a minimal amount due to gasification. Trubetskaya et al. [19,32] observed that increasing temperature up to 1000 ºC had a favourable effect on volatile yield, whereas beyond this temperature, the influence was negligible for the samples used. The authors also reported that a residence time of 2 s at the plateau temperature was sufficient to remove all the volatiles.

The effect of particle size was evaluated by experimenting different size ranges at 4 and 5 s residence times. The results indicate that particle size does not limit the devolatilization of the particle if given enough time. Large particle size might prevent heat transfer during the two early stages of the pyrolysis, but at 4 seconds residence time the values are within a 5% difference range from 300-500 μm to 1120-1400 μm . Woody biomass has enough porosity to allow the gases produced during pyrolysis to flow easily and exit the particle [33]. The typical needle shape, with large aspect ratio of the woody biomass particles might also help, allowing an effective heat transfer towards the center of the particle even for short residence times.

The volatile yield under the 4 seconds residence time 1600 ºC was obtained for all samples and results are given in table 2. As expected, higher values of volatile yield than those from the proximate analysis were obtained for all samples. OW was the only sample for which the volatile yield increases only slightly (+1.5%); this sample seems to be little affected by the higher temperatures. These result are in agreement with previous experiments such as reactivity analysis [34] or combustion experiments under different conditions [35] where the olive waste biomass showed to be less affected than any other fuels by the main conditions that influence the combustion. Both woody biomass samples showed a clear volatile yield increase (+6.7% and +6.9% for WP and BP respectively), which is a quite moderate increment on the already high values of volatile yield shown by proximate analysis.

**Figure 3. High temperature volatile yield versus proximate analysis volatile yield.**

Coal C is a poor quality coal (high ash), with low volatile matter. The volatile yield obtained in the HTWM is 13.6 % which is two-fold the value obtained by proximate analysis. Coal A reached a 53% volatile yield on the HTWM which is an increase of 13 % over the 39 % volatile from the proximate analysis. This value is within the range for similar coals studied by Man et al. [14]. The high increase of +26.2% on volatile yield was obtained for coal B, which is almost double the value from proximate analysis. Coals A and B have a high ash content, at high temperatures, the inorganic mater can also decompose releasing gases that can increase the volatile yield value obtained. As occurred in other previous studies, these results show that a poor linear relationship between high temperature volatile yield and proximate analysis volatile yield can be established (Figure 3). There are clear outliers, so it is not possible to predict the real volatile yield on pulverized fuel boilers from proximate analysis.

The temperature of the mesh during the experiments and therefore the temperature of the fuel chars has a great influence on the pyrolysis process. Coal B was also studied at a lower temperature of 1200 ºC. Under this conditions the coal volatile yield was 47% which is 6.5% less than the volatile yield at 1600 ºC and 19.6% more than the proximate analysis value.

* 1. **Nitrogen Partitioning**

The char obtained from the experiments carried out on the biomass and coal samples were analysed for total nitrogen content in order to determine the nitrogen partitioning. This analysis was done by triplicate for each char sample to evaluate the variability, obtaining a 12% standard error. The data obtained can be useful to understand the differences in biomass and coal combustion performance and emissions. WP biomass sample was exposed to different residence times at 1600 ºC and results are presented in Figure 4.

**Figure 4 . Char Nitrogen content at different residence times for WP biomass.**

Nitrogen is proportionally released in the volatile yield as the pyrolysis progresses, however the char is enriched in nitrogen during the early stages of pyrolysis. This is due to the high amount of light gases such as CO, CO2 and H2O from the carbohydrates [36]. The partitioning of nitrogen between the volatiles and char of biomass is highly dependent on the decomposition routes of the proteins and reactions between proteins and carbohydrates. Darvel et al. [4] studied different model compounds for biomass nitrogen release and found that the structure of the amino acids has a significant effect on the nitrogen transformation. The different nitrogen compounds were observed to follow two routes; first one leading to NH3 and char formation. The second route evolves towards volatile cyclic amides and leads to HCN formation. Some compounds will release nitrogen at early stages and other lead to nitrogen fixation on the char. This explains why for low residence times it is possible to have an increase on N content in the char. The values for increasing residence time after 3 seconds, progress towards lower nitrogen content in an almost linear tendency. Enrichment in char-N at lower temperatures was observed by Brower et Brown [37] under gasification conditions, observing a maximum at 750ºC. Higher nitrogen was retained in pinewood char than sawdust especially at 900 °C implying that biomass compounds and temperature affects nitrogen distribution during pyrolysis. The nitrogen content of the char means that part of it is fixed on stable compounds and functionalities in the structure of the biomass chars, as it remains having nitrogen in advanced pyrolysis chars.

For the high temperature volatile yield study, three different size ranges (300-500 μm, 500-710 μm and 1120-1400 μm) were studied in order to check the influence that this may have on the nitrogen release. Differences of only 0.02 % were found on the nitrogen of the chars content for the size fractions studied, i.e. no significant difference in N-release with particle size. This could be due to the properties of biomass fuels such as thermal conductivity and pore distribution of fuels and chars. It implies an effective heat transfer from the surface towards the centre of the particle enabling devolatilizaton throughout the whole particle and mass transfer rates that allow the volatile compounds to reach the surface of the particle easily even in the short residence time.

**Table 2. Volatile yield and Volatile nitrogen results from the different samples.**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | **OW** | **BP** | **WP** | **Coal A** | **Coal B** | **Coal C** |
| **proximate analysis Weight % db** | **ash content** | 7.6 | 4.2 | 0.8 | 1.5 | 34.1 | 34.6 |
| **volatile content** | 74 | 76 | 83.7 | 39.5 | 27.4 | 6.3 |
|  | **Fuel N content** | 1.48 | 0.19 | 0.15 | 2.2 | 0.99 | 0,86 |
| **High temperature wire mesh 1600 ºC 4s** | **Volatile yield** | 75.5 | 82.7 | 90.6 | 52.8 | 53.6 | 13.6 |
| **%wt N in char** | 0.38 | 0.15 | 0.17 | 0.20 | 0.63 | 0.29 |
| **% Volatile N** | 93.8 | 87.1 | 87.7 | 95.7 | 70.4 | 72.9 |

As summarized in table 2, all values of volatile nitrogen and volatile yield were high as expected for the conditions of the experiments, although there were differences among the samples. Both woody biomass reached similar values of volatile nitrogen of over 87%. OW released 94% of nitrogen as volatile, but still retained a higher content in the char (0.37 wt%) compared to the other biomass due to the higher initial nitrogen content in the fuel. Differences among the biomass samples on their nitrogen release under pyrolysis can be explained by the fact that nitrogen fuel compounds may be forming different compounds that determine different precursor materials and therefore chemical stability of the nitrogen in the char. Wood biomass is mainly formed by hemicellulose, cellulose and lignin. Olive waste has higher amount of polysaccharides, proteins, lignin and relatively high amount of fatty acids [38]. The nitrogen present in some amino acids can increase the proportion of nitrogen in the char. However, there is not a single amino acid present in the olive waste that links a direct relationship between nitrogen retention in char with a single compound. According to the literature [39], both asparagine and glutamine are found on considerable amount on the olive waste. Blends of these compounds with cellulose and glucose were previously observed to lead to significative nitrogen retention in the char during pyrolysis [4]. Some ash elements can also act as intermediate compounds during pyrolysis reactions, influencing the char yield and nitrogen retention. Olive waste has higher concentrations of alkali elements and higher ash content than the woody samples that may increase the volatile release.

The differences in nitrogen partitioning during high temperature pyrolysis helps understand the differences in NOx formation when cofiring coal and biomass. As observed in many cofiring studies [12, 40, 41] the addition of biomass in the fuel blend reduces the NOx production even for similar nitrogen content on the elemental analysis on the fuel, the different nitrogen partitioning will produce different NOx precursors. The release of nitrogen compounds in the presence of coal volatile matter reduces NOx emissions due to the reducing effect of coal volatiles. Biomass also produces lower flame temperatures and moderate the temperature during coal pyrolysis, resulting on a more progressive pyrolysis that benefit a higher nitrogen release from coal. Thus for the fuels study, it can be stated that biomass combustion on deep air stage is less likely to produce NOx formation due to the release of the nitrogen as volatile nitrogen.

The temperature of the pyrolysis conditions has been found as a main parameter for the partitioning of nitrogen from the fuel. The nitrogen content for coal B char obtained at 1200ºC was 0.81 wt% compared to 0.63 wt% nitrogen in the char obtained at 1600ºC . The difference cannot be attributed only to higher volatile yield; at that severely high temperature, tertiary pyrolysis reactions are releasing nitrogen components that were formerly fixed in molecules stable at moderate to high temperatures [4, 42]. As described in the literature [43] nitrogen compounds are present in heterocyclic compounds in coal. During pyrolysis cracking reactions promote a progressive release of part of the nitrogen in the volatiles while part of nitrogen is fixed as char-N. The rapid pyrolysis condition favours the retention of nitrogen in the char [44]. Biomass fuels not only release fuel-nitrogen as volatile-N, but as biomass release much higher amount of volatile yield, the overall amount of char-N is much higher for the coals studied than the biomass.

These values suggest that the nitrogen content vary during the pyrolysis, having a maximum at an intermediate temperature and lowering its concentration at the higher temperatures.

**Figure 5. Volatile Nitrogen versus volatile yield obtained for BP and OW biomass.**

As can be inferred from previous results, some of the results for BP and OW samples given in figure 5 show a strong relationship between the volatile nitrogen and the volatile yield released. This relationship might not be that clear for primary pyrolysis but is almost linear for advanced fuel chars.

1. **Conclusions**

High temperature pyrolysis was achieved under helium atmosphere for a range of biomass and coals. The volatile yield increases with residence time up to 4 s. For longer residence times, similar volatile yields were obtained. Volatile yields obtained on the high temperature wire mesh were higher than proximate analysis values for 4 s residence time for all samples. Results show a moderate increase of 6.9 % of the volatile yield for woody biomass and 6.7% for steam torrefied wood that already have high values on proximate analysis. A slight increase of 1.5% was observed on the volatile yield for the olive waste. A greater increase in the volatile yield was observed for all coals. Bituminous coals A and B raised from 39.5% and 27.4% of volatile matter on proximate analysis to 52.8% and 53.6% volatile yield (dry basis) respectively. Anthracite coal C increased from 6.3% on proximate analysis to 13.6% on the volatile yield obtained. Obtaining compared with proximate analysis values. A correlation between proximate analysis and high temperature volatile yield was not validated for all samples. Therefore, it is not possible to predict the real volatile yield in pulverized fuel boilers from proximate analysis values.

Nitrogen is proportionally released with volatile matter; although the evolution is not linear for the entire pyrolysis process. Nitrogen content at 3 seconds residence time was observed to be higher than initial fuel content, having a proportional decrease afterwards linked to progressive volatile mater release. The biomass samples release most of the nitrogen as volatile-N. The proportion of volatile-N for 4s residence time up to a temperature of 1600 ºC was: 94 % OW; 87 % BP; 88 % WP. For the coals, the volatile nitrogen was more widely variable depending on the coal sample being 95.7%, 70.4% and 72.9% volatile-N for coals A,B, and C respectively. The observation that there is lower nitrogen content, higher volatile yield and high volatile-N for the woody biomass suggests a much lower total nitrogen amount retained in woody biomass char compared to coals. This leads to the conclusion that combustion of woody biomass fuels, compared to coals, are less likely to form NOx emissions in pulverized fuel boilers.

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**References**

[1] Directive 2010/75/eu of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control) (Recast) (2010) *Official J Eur Union*, (L334), 17-119.

[2] Yan Q, Yang R, Zhang Y, Umar A, Huang Z, Wang Q. A comprehensive review on selective catalytic reduction catalysts for NOx emission abatement from municipal solid waste incinerators. Environmental Progress and Sustainable Energy 2016;35:1061-1069

[3] Fan W, Li Y, Guo Q, Chen C, WangY, Coal-nitrogen release and NOx evolution in the oxidant-staged combustion of coal. Energy 2017;125:417-426 [4] Darvell L, Brindley C, Baxter XC, Jones JM, Williams A. Nitrogen in biomass char and its fate during combustion: A model compound approach. Energy and Fuels 2012;26:6482-6491

[5] Goulding KWT, Bailey NJ, Bradbury NJ, Hargreaves P, Howe M, Murphy DV, Poulton PR, Willison TW. Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes. New Phytologist 1998; 139: 49–58.

[6] Darvell L, Jones JM, Gudka B, Baxter XC, Saddawi A, Williams A , Malmgren A. Combustion properties of some power station biomass fuels. Fuel 2010;89: 2881-2890

[7] McNamee P, Darvell LI, Jones JM, Williams A. The combustion characteristics of high-heating-rate chars from untreated and torrefied biomass fuels. Biomass and Bioenergy 2015; 82:63-72

[8] Axworthy AE, Dayan VH, Martin GB. Reactions of fuel-nitrogen compounds under conditions of inert pyrolysis. Fuel 1978;57:29-35.

[9] Tan L, Li C. Formation of NOx and SOx precursors during the pyrolysis of coal and biomass. Part I. Effects of reactor configuration on the determined yields of HCN and NH3 during pyrolysis Fuel 2000;79:1883–1889

[10] Álvarez L, Gharebaghi M, Jones JM, Pourkashanian M, Williams A, Riaza J, Pevida C, Pis JJ, Rubiera F. Numerical investigation of NO emissions from an entrained flow reactor under oxy-coal conditions. Fuel Processing Technology 2012;93:53-64

[11] Loo SV, Koppejan J. The Handbook of Biomass Combustion and Co - firing. vol. 1. 2015. doi:10.1017/CBO9781107415324.004.

[12] Riaza J, Gil MV, Álvarez L, Pevida C, Pis JJ, Rubiera F. Oxy-fuel combustion of coal and biomass blends. Energy 2012;41:429-435

[13] Munir S, Nimmo W, Gibbs BM. “The effect of air staged, co-combustion of pulverised coal and biomass blends on NOx emissions and combustion efficiency” Fuel 2011;90:126–135.

[14] Man C, Gibbins J, Witkamp J, Zhang J. Coal characterisation for NOx prediction in air-staged combustion of pulverised coals. Fuel 2005;84:2190–2195,

[15] Wagner DR, Whitty KJ. A pulse-width modulation controlled wire-mesh heater apparatus for investigation of solid fuel pyrolysis. Review of Scientific Instruments 2012;83:115-116

[16] Di Nola G, de Jong W, Spliethoff H. The fate of main gaseous and nitrogen species during fast heating rate devolatilization of coal and secondary fuels using a heated wire mesh reactor. Fuel Processing Technology 2009;90:388-395

[17] Drummond, A.-R.F., Drummond, I.W. Pyrolysis of Sugar Cane Bagasse in a Wire-Mesh Reactor. Industrial and Engineering Chemistry Research 1996;35:1263-1268

[18] Gibbins J, Kandiyoti R. Coal Pyrolysis Yields from Fast and Slow Heating in a Wire-Mesh Apparatus with a Gas Sweep. Energy and Fuels 1988;2:505-511

[19] Trubetskaya A, Jensen PA, Jensen AD, Steibel M, Spliethoff H, Glarborg P. Influence of fast pyrolysis conditions on yield and structural transformation of biomass chars. Fuel Process Technol 2015;140:205–14.

[20] Le Manquais K, Snape C, McRobbie I, Barker J, Pellegrin V. Comparison of the combustion reactivity of TGA and drop tube furnace chars from a bituminous coal. Energy and Fuels 2009;23:4269–77.

[21] Tremel A, Spliethoff H. Gasification kinetics during entrained flow gasification - Part I; Devolatilisation and char deactivation. Fuel 2013;103:663–71.

[22] Farrow TS, Sun C, Snape CE. Impact of CO2 on biomass pyrolysis, nitrogen partitioning, and char combustion in a drop tube furnace. J Anal Appl Pyrolysis 2015;113:323–31.

[23] Kidena K, Hirose Y, Aibara T, Murata S, Nomura M. Analysis of nitrogen-containing species during pyrolysis of coal at two different heating rates. Energy and Fuels 2000;14:184-189

[24] Saeed M, Andrews G, Phylaktou H, Gibbs B. Global kinetics of the rate of volatile release from biomasses in comparison to coal. Fuel 2016;181:347–357.

[25] Fletcher TH, Kerstein AR, Pugmire RJ, Solum M, Grant DM. A chemical percolation model for devolatilization: summary 2015;1:1–66.

[26] BS EN ISO 18134-3:2015 Solid biofuels. Determination of moisture content. Oven dry method. Moisture in general analysis sample

[27] BS EN ISO 18123:2015 Solid biofuels. Determination of the content of volatile matter

[28] BS EN ISO 18122:2015 Solid biofuels. Determination of ash content

[29] BS EN ISO 16948:2015 Solid biofuels. Determination of total content of carbon, hydrogen and nitrogen

[30] BS EN ISO 18125:2017 Solid biofuels. Determination of calorific value

[31] Riaza J, Gibbins J, Chalmers H. Ignition and combustion of single particles of coal and biomass. Fuel 2017;202:650–655.

[32] Trubetskaya A, Jensen PA, Jensen AD, Garcia Llamas AD, Umeki K, Glarborg P. Effect of fast pyrolysis conditions on biomass solid residues at high temperatures. Fuel Process Technol 2016;143:118–29.

[33] Gil MV, Riaza J, Álvarez L, Pevida C, Rubiera F. Biomass devolatilization at high temperature under N2 and CO2: Char morphology and reactivity. Energy 2015;91:655–62.

[34] Magalhães D, Kazanç F, Riaza J, Erensoy E, Kabaklı Ö, Chalmers H. Combustion of Turkish lignites and olive residue: Experiments and kinetic modeling. Fuel 2017;203:868-876

[35] Riaza J, Khatami R, Levendis YA, Álvarez L, Gil MV, Pevida C, et al. Combustion

of single biomass particles in air and in oxy-fuel conditions. Biomass Bioenergy 2014;64:162–174.

[36] Niksa S. Predicting the rapid devolatilization of diverse forms of biomass with bio-flashchain. Proc Combust Inst 2000;28:2727–33.

[37] Broer KM, Brown RC. The role of char and tar in determining the gas-phase partitioning of nitrogen during biomass gasification, Applied Energy 2015;158:474-483

[38] Saiz-Jimenez C, De Leeuw JW, Gomez-Alarcon G. Sludge from the waste water of the olive processing industry: a potential soil fertilizer? Science of The Total Environment 1987;62:445-452

[39] Manoukas AG, Mazomenos B, Meropi A, Patrinou J. Amino Acid Compositions of Three Varieties of Olive Fruit. J Agric Food Chem. 1973;21:215-217.

[40] Sahu SG, Chakraborty N, Sarkar P. Coal–biomass co-combustion: An overview. Renewable and Sustainable Energy Reviews 2014;39:575-586.

[41] Battista J J, Hughes EE, Tillman DA. Biomass Cofiring at Seward Station. Biomass Bioenergy 2000;19:419-427.

[42] Zhang X., Sun S, Sun R, Li X, Zeng G. Effects of bias combustion on volatile Nitrogen transformation. Asia-Pacific Journal of Chemical Engineering 2010;5:473-478

[43] Jones JM, Pourkashanian M, Williams A, Rowlands L, Zhu Q, Thomas KM. Conversion of char nitrogen to NO during combustion. Journal of the Energy Institute 2004;77:82:89

[44] Jones JM, Bridgeman TG, Darvell LI, Gudka B, Saddawi A, Williams A. Combustion properties of torrefied willow compared with bituminous coals. Fuel Processing Technology 2012;101:1-9