



## Full Length Article

# Experiments and modelling of NO<sub>x</sub> precursors release (NH<sub>3</sub> and HCN) in fixed-bed biomass combustion conditions

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## ABSTRACT

There is a need to reduce NO<sub>x</sub> emissions, which can only be achieved through a detailed understanding of the mechanisms for their formation and reduction. In this work the release of the NO<sub>x</sub> precursors, NH<sub>3</sub> and HCN, for different fuels is experimentally analysed and modelled in typical fixed-bed combustion conditions. It is shown that NH<sub>3</sub> and HCN are released during the main devolatilization phase and the NH<sub>3</sub>/HCN ratio increases for fuels with a higher nitrogen content. A simplified two-steps model for their release is presented. The model can predict with a reasonable accuracy the release for fuels with a low nitrogen content, however deviations are present for fuels with a high nitrogen content, which probably arise due to a reduction of NH<sub>3</sub> and HCN taking place already in the bed.

## 1. Introduction

Due to the climate change, there is a steadily growing demand for CO<sub>2</sub> neutral supply of energy. Heat (and power) production by combustion of solid woody biomass is already a consolidated technology. However, impurities emitted during biomass combustion, such as nitrogen oxides (NO<sub>x</sub>), fine particulate matter (PM), volatile organic compounds (VOC) or carbon monoxide (CO), are main air pollutants [1]. There is an increasing awareness regarding the need to reduce air pollution, which damages our health and the environment, and a consensus among policy-makers that more action is needed to make further progress in emissions reduction.

Nitrogen oxides are the emissions with a higher environmental impact based on a lifecycle assessment on wood combustion in automatic furnaces [2]. NO<sub>x</sub> emissions can be produced by thermal-NO<sub>x</sub>, prompt-NO<sub>x</sub> and fuel-NO<sub>x</sub> mechanisms. Fuel-NO<sub>x</sub> is the most relevant pathway in biomass combustion, due to the relatively low temperatures that are commonly achieved (900–1000 °C with peak values up to 1300 °C) do not activate to a significant extent the formation of thermal-NO<sub>x</sub> and prompt-NO<sub>x</sub> [3]. Fuel-NO<sub>x</sub> emissions depend on the nitrogen content of the fuel as well as on the combustion process conditions [2–7]. Air staging strategies have been developed in order to reduce NO<sub>x</sub> emissions. However, current emissions are still high and besides, the range of employed biomass feedstock is being broadened, including fuels with lower price but a higher nitrogen content. Therefore, there is a need to reduce NO<sub>x</sub> emissions, which can only be

achieved through a detailed understanding of the mechanisms for their formation and reduction.

Proteins are the main source of fuel-N in common biomass sources, such as wood [8]. It was reported that 60–80% of nitrogen in biomass is present as protein-N in most of the samples in a study with 15 woody and agricultural biomasses, with even a higher content in the other 3 samples [9]. A protein nitrogen content close to 90% has been reported for sewage sludge [10]. Other fuel-N sources, such as inorganic ammonium, pyrrole and pyridine, are commonly present in biomass at much lower concentrations [10]. This is not the case for coal, where pyrrolic (five-rings) and pyridinic (six-rings) are the main nitrogen functionalities, with smaller amounts of quaternary nitrogen and amines [4].

The major routes for fuel-NO<sub>x</sub> formation during biomass combustion are shown in Fig. 1 [11,12]. NH<sub>3</sub> and HCN (and to a minor extent HNCO) are the main NO<sub>x</sub>-precursor species that are produced during biomass pyrolysis. They are however not mainly directly released from primary pyrolysis of proteins. The main primary pyrolysis product of proteins are amides, such as the cyclic DKP (diketopiperazines), which are tar-N compounds. There is however a great variety of tar-N compounds, being other families present [13]. Secondary tar cracking reactions of tar-N compounds produce gas-N species: NH<sub>3</sub>, HCN and, in a minor extent, HNCO [14,15], by cracking of amine N-tar (primary tars) at temperatures lower than 500 °C and mainly by cracking of heterocyclic and nitrile N-tars (secondary tars) at higher temperatures (> 500 °C) [10,16]. Furthermore, a significant fraction of fuel-N is

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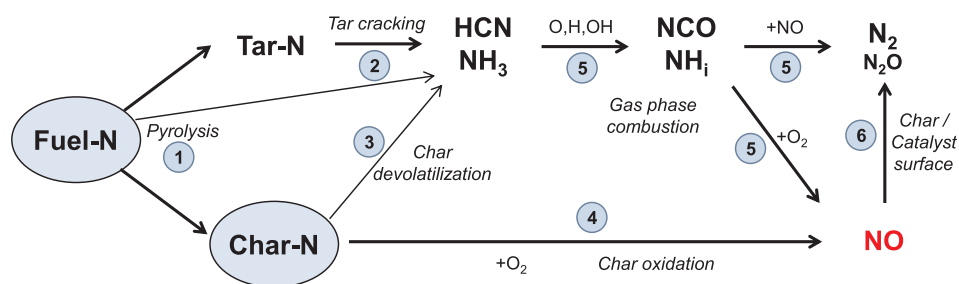


Fig. 1. Major routes of NO-fuel formation during biomass combustion, inspired in [11,12].

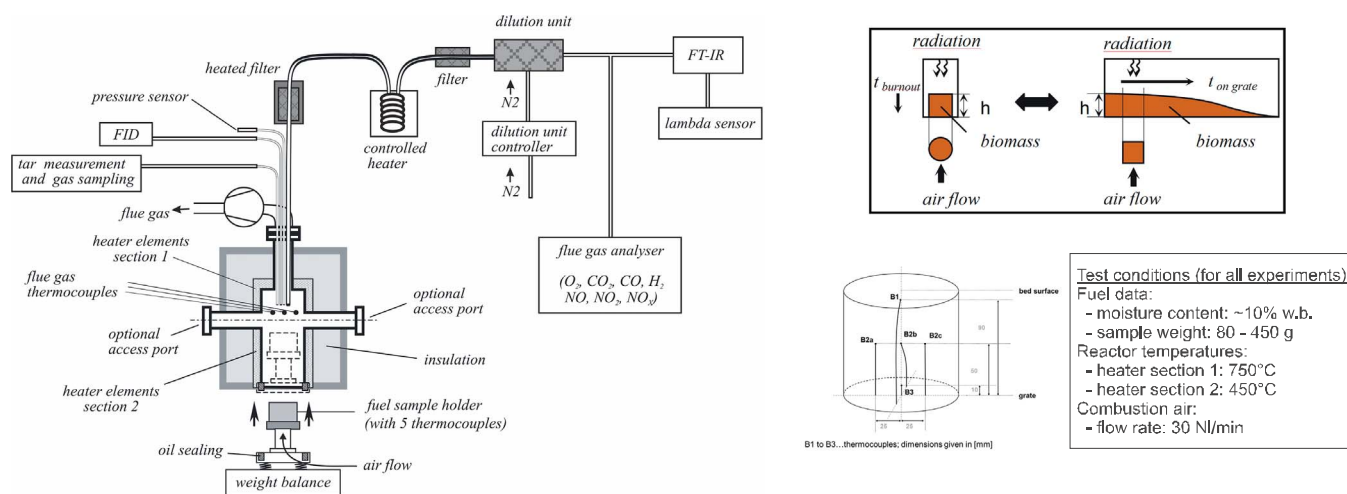


Fig. 2. Scheme of the lab-reactor setup.

retained in char during pyrolysis [8]. Low temperature chars have a similar N/C ratio than the original biomass, but, as opposite to coal, there is a significant loss of nitrogen in char when temperature is increased to 800 °C and over [11,17].

Besides primary pyrolysis, tar cracking and char devolatilization reactions (R1, R2 and R3 in Fig. 1), which can take place in an inert atmosphere, char oxidation (reaction R4) with O<sub>2</sub> produces mainly NO (N<sub>2</sub>O can be as well produced) and gas phase oxidation of NO<sub>x</sub>-precursors (reactions R5) leads mainly to NO and N<sub>2</sub>, besides N<sub>2</sub>O which can be produced from HCN. The presence of NO promotes the production of N<sub>2</sub>, which leads to a reduction in the conversion rate of fuel-N to NO for fuels with a higher nitrogen content [7], because the concentration of nitrogen species in the gas phase, including NO, increases. Furthermore, reducing conditions promote the formation of N<sub>2</sub>, therefore air staging strategies are required for the reduction of NO<sub>x</sub> emissions. Finally, char and inorganics can catalyse several reactions, including the reduction of NO to N<sub>2</sub> (reaction R6 in Fig. 1) as well as the conversion of HCN to NH<sub>3</sub> [11]. Char-N conversion to NO in single particle char combustion can be lower than 50% for a temperature of 1300 K and a diameter of 8 mm due to NO reduction on the char surface [18].

Despite being quite complex, the gas phase oxidation NO<sub>x</sub> chemistry is well understood. However, this is not the case for the fuel-N release [5]. The ratio between the release during pyrolysis of HCN and NH<sub>3</sub>, which are main NO<sub>x</sub> precursors and are mainly produced from cracking of tar-N species, varies widely for biomass. Both NH<sub>3</sub> and HCN have been reported as the major gas-N product for different species [15]. Pyrolysis of bituminous coals produces mainly HCN, while more NH<sub>3</sub> evolves in general from lower rank coals and biomass [4]. It has been reported that the NH<sub>3</sub>/HCN both decreases [19] and increases [15,20] with a higher nitrogen content in the fuel. Moreover, high heating rates increase HCN production, while low heating rates as well as bigger particle sizes lead to more NH<sub>3</sub> production. This is attributed to

enhanced HCN hydrogenation on the char surface to NH<sub>3</sub>, as HCN diffuses out of the particle, for both coal and biomass [4,21,19]. There are as well fundamental studies with proteins or amino acids, however their results are difficult to extrapolate to real applications, as the product composition of protein pyrolysis is significantly influenced by the presence of cellulose, hemicellulose and lignin, as well as by inorganics [9,15]. Moreover, as previously stated, the particle size and gas composition have a major influence on the final products. Therefore, it is recommended to conduct experimental work with biomass in conditions which resemble the final application.

The objective of this work is to experimentally analyze and model the release of the NO<sub>x</sub> precursors, NH<sub>3</sub> and HCN, for different fuels in typical fixed-bed combustion conditions. Advances in understanding of NO<sub>x</sub> precursors release shall contribute to the development of combustion technologies with lower NO<sub>x</sub> emissions. For this purpose, experimental results with a lab-scale reactor from Bioenergy 2020+ will be employed. This reactor has been designed for simulating biomass combustion on a grate and results with selected feedstock have been already presented [6,20]. In this work, correlations will be developed with the previous and novel results and a simplified model for the release of NO<sub>x</sub> precursors will be presented. The experimental set-up will be presented in Section 2, the experimental results and discussion in Section 3 and the modelling in Section 4, to finally present the conclusions.

## 2. Experimental setup

The lab-scale reactor (see Fig. 2) is a discontinuously operated cylindrical pot furnace which has been designed for simulating fixed-bed biomass combustion on a grate. Biomass is introduced into a cylindrical holder (100 mm height and 95 mm inner diameter), occupying all the volume. The holder is inside an electrically heated cylindrical retort. The initial sample mass is between 80 and 450 g, depending on the fuel

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