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An overview of nitrogen oxides emissions from biomass combustion for domestic heat production

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Abstract

In order to fulfill the EU's climate and energy goals, the heating and cooling sector must cut its use of fossil fuels. Solid biomass can constitute an alternative to fossil fuels as a renewable and carbon-neutral source of energy but there are some aspects to biomass combustion in small scale domestic appliances that can compromise the environmental sustainability of this renewable energy source in terms of burden on air quality. The priority pollutants in this respect are particulate matter (PM) and nitrogen oxides (NOx). While PM emissions are often discussed, NOx emissions from domestic heating appliances are relatively less in the center of attention. The aim of the present study is to review the literature regarding the NOx emissions from this emission source discussing the main formation mechanisms and the state-of-the-art control techniques, as well as the influence of fuel composition (especially fuel bound nitrogen), heating appliance type and operating conditions with the help of the gathered experimental emission factors data. The review crosslinks several aspects usually treated separately in scientific papers (e.g., only laboratory tests with basic theory or only field tests on emission levels etc.), providing thus a quick reference tool to the state-of-the-art knowledge on this topic.

Highlights

- NOx emissions from biomass combustion mainly from the fuel bound nitrogen
- Average emission factors in the range of 67-79 mg/MJ for woody biomass combustion
- Hard times for the introduction in the market of N-rich alternative solid biofuels
- Research on NOx abatement technologies in small scale heating appliances is needed

Keywords

Nitrogen oxides; emission factors; domestic heating; fuel bound nitrogen; char oxidation; air-staging; NOx control; biomass combustion.

Word Count: 6135

1. Introduction

EU adopted the binding renewable energy target of at least 32% by 2030 which requires member states to increase their proportion of renewable heat. In order to fulfil the EU's climate and energy goals, the heating and cooling sector must cut its use of fossil fuels. Biofuel use gains thus a crucial importance in the EU strategy for heating and cooling together with other renewable heating and cooling technologies.

Solid biomass is potentially interesting given the high share (82%) in renewable heat production and the advantage of the lower energy price with respect to fossil fuels. It can play an important role in CO_2 emissions mitigation and be an alternative to fossil fuels as a renewable and carbon-neutral source of energy but there are some aspects to biomass combustion for domestic heat production that can compromise the environmental sustainability of this renewable energy source in terms of burden on air quality. The priority pollutants in this respect are particulate matter (PM) and nitrogen oxides (NOx).

PM emissions are often discussed and pointed out as a major contributor to the air pollution in lower atmosphere [1]. Since there are frequent exceedances of the PM air quality limit values, more and more restrictions are in act including ban of less efficient biomass heating appliances. NOx emissions on the other hand are relatively less in the centre of attention even though life cycle assessment studies indicate that a great part (40%) of the environmental impact of a modern automatic wood furnace may be associated with NOx emissions [2].

The present review aims to address key issues regarding NOx emissions from domestic heating appliances (indicatively <50 kW) fed with solid biomass in different forms (e.g., densified biomass such as pellets, firewood). First, various studies investigating the NOx formation from biomass combustion are synthesized to prospect the main aspects regarding the formation and reduction of NOx since a correct understanding of the parameters regulating NOx release contribute to the development of combustion technologies with reduced emissions. Second, primary control mechanisms applied to domestic heating appliances are presented and discussed with particular attention to air-staging as it is the main control method applied to non-industrial appliances. Given the dominant influence of fuel bound nitrogen (fuel-N) on NOx emissions, this aspect is specifically addressed. The effect of other fuel components is also discussed. Finally, given the important role that emission factors play in the quantitative estimations of the emission source contributions to the atmospheric levels, a review of literature experimental emission factors is reported and the results are discussed in terms of the influence of heating appliance type and operating conditions. The paper is concluded with a quick a comparison of biomass combustion for domestic heat production with major fossil fuel alternatives and the assessment of the gathered emission factors in the framework of national and European regulatory framework.

To the authors' knowledge this is the first review paper on NOx emissions from small scale (50 kW) domestic heating appliances burning solid biomass which crosslinks several aspects usually treated separately in scientific papers (e.g., only laboratory tests with basic theory or only field tests on emission levels etc.), providing thus a quick reference tool to the state-of-the-art knowledge on this topic.

2. Methodology

72 scientific articles (predominantly from peer-reviewed journals, few from conference papers) and 15 other type of documents (i.e., web pages, databases etc.) were consulted in order to give an overview of NOx emissions from small scale biomass combustion appliances. Table 1 summarizes the consulted scientific papers in terms of research area.

Table 1. Summary of the consulted scientific papers and the breakdown for the research area

Main research area	Total number of articles	References
NOx formation mechanisms	13	[12-24]
NOx control techniques	19	[2, 20, 25-41]
Fuel characterization	10	[2-11]
Fuel indexes and NOx prediction from fuel-bound nitrogen	5	[28, 42-49]
Experimental NOx emission factors	41	[6, 7, 9, 39, 41, 47, 50, 52-69, 71-86]

The papers were basically representative of European residential heating appliances (indicatively <50 kW). Few laboratory combustor studies discussing the fuel effects, or the influence of combustion air control were also included. The investigated appliances included automatically fed pellet boilers, multi-fuel boilers, wood log boilers, automatic or batch-fired room heaters (i.e., local space heaters), heat accumulating and slow heat release appliances, fireplace inserts, open fireplaces. Greater part of automatic boilers was equipped with air-staging solutions. Some were combined with heat storage buffer tanks. Most of the room heaters resulted characterised by a single common chamber for the thermal decomposition and combustion of formed gaseous flammable products (single stage combustion). Very few were equipped with specific secondary air inlets (diverse from window flush air). The biomass used comprehended wood and woody biomass, agriculture residues (husks, pits, shells, grains, pruning residues etc.), herbaceous biomass (grasses and straws), treated wood and wood industry residues, and food industry residues. The fuel was fed either as firewood (with and without bark) or in a densified form such as pellets or briquettes.

The collected emission factors were categorized in terms of heating appliance type (automatic vs. manually fed (i.e., batch working) appliances) and the origin of the biomass fuel (woody vs. non-woody biomass). Data analysis mainly consisted of the summary of experimental emission factors through descriptive statistics of the grouped data (i.e., per appliance and fuel type) and the graphical representation in the form of boxplots. Bootstrap confidence intervals (95%CI) were also calculated for group averages to have an idea whether there could be a significant difference between the investigated groups: largely overlapping confidence intervals would suggest a lack of statistical significance in the observed differences.

The main parameters of interest were the experimental NOx emission factors, biomass fuel characterization (e.g., fuel-bound nitrogen, ash content, heating value), heating appliance characteristics and operational details. The gathered data, where necessary, was pre-processed as follows prior to statistical analyses to summarize the results or to investigate the fuel-N to NOx relationship:

- NOx (NO+NO_2) emissions are all expressed as NO_2 equivalents. Few studies reported only NO emission factors, in this case NOx emissions were calculated based on NO emissions (expressed as NO_2) only: this implies a slight underestimation in the emission factors;
- NOx data provided in the form of concentration values (e.g., mg/m^3 NTP dry gas 13%O_2) were converted to emission factors (e.g., mg/MJ) following the procedure indicated in European Air Pollutant Emission Inventory Guidebook [3];
- The lacking fuel characterization data, where necessary, were filled-in with inherent literature values provided by [2, 3, 4, 5, 6, 7, 8, 9, 10, 11] for different biomass fuels.

The conversion of fuel bound nitrogen into nitrogen in NOx emissions ($X_{NOx\text{-}N/fuel\text{-}N}$) was estimated as the ratio of the measured emission factors to the theoretical maximum amount of NOx coming from the complete oxidation of the fuel bound nitrogen.

3. NOx formation in biomass combustion

There are three gas phase reaction mechanisms for NOx formation in combustion processes [12]: thermal NOx mechanism (atmospheric nitrogen oxidation due to high temperatures>1300°C), fuel NOx mechanism (oxidation of fuel-N) and prompt NOx mechanism (due to reaction of CHi-radicals with atmospheric nitrogen in the flame front). While thermal and prompt NOx mechanisms can be significant for fossil fuel combustion applications, in biomass combustion, the temperature in the combustion chamber is typically below 1300 °C (900 °C-1000 °C with peak values up to 1300 °C), therefore, NOx formation is dominated by the fuel-N mechanism.

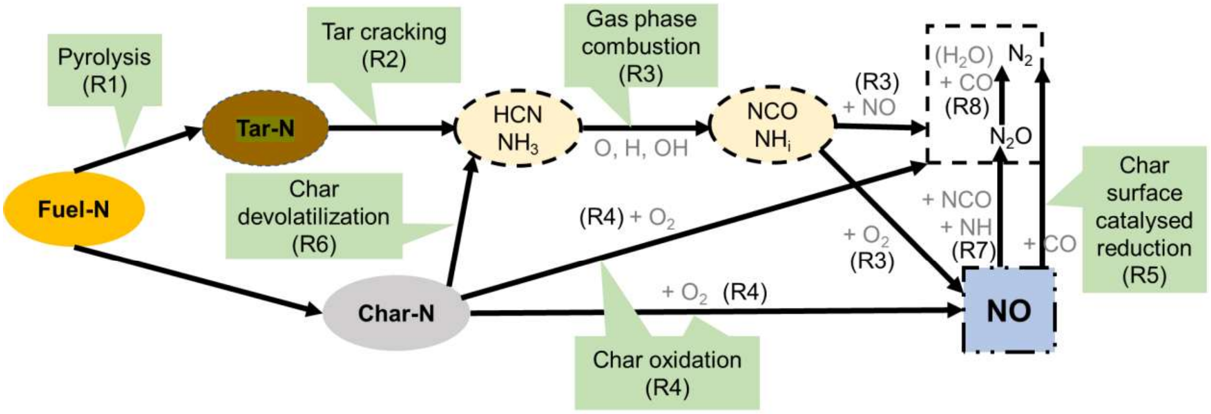

Fig. 1. Major routes of NOx formation from fuel bound nitrogen during biomass combustion (Adapted from [21, 22])

The fuel-N mechanism (Fig. 1) in biomass combustion is complex and involve both formation and reduction of NO with overlapping homogeneous and heterogeneous reaction paths [13]. The conversion of fuel-N starts with the pyrolysis (Reaction R1 in Fig. 1) of biomass material when a part of the fuel-N is released as tar-N and then converted to volatile-N (NH_3, HCN, and minorly HNCO) through tar-cracking (Reaction R2). However, a part of fuel-N remains in the char matrix (char-N) during pyrolysis. Both volatile-N and char-N contribute to NOx emissions. Nonetheless, a greater part of fuel-N (around 60%-90%) is reported to be released as volatile-N (called also NO precursors or N-intermediates by some authors) for different biomass feedstocks and waste biomass [14, 15, 16, 17]. The distribution of the fuel-N between the volatiles and the remaining char is roughly proportional to the volatile matter in the fuel [18] and it is important because while the conversion of volatile-N can be reduced by air control, char-N conversion into NOx emissions is more difficult to overcome [19].

The volatile-N are converted into NH_i radicals through gas phase combustion (Reaction R3). These radicals can either be oxidized (Reaction R3) to NO in oxygen rich conditions or can work as a reduction agent and reduce the already formed NO to N_2O (Reaction R7); thus, they are the driving force in NOx reduction [20]. The presence of NO promotes the production of N_2 which leads to a reduction in the conversion rate of fuel-N to NO for fuels with a higher fuel-N because the concentration of gaseous N-species (including NO) increases [21].

The char-N on the other hand is oxidized to NO in the presence of oxygen (Reaction R4). The initially formed NO is partly reduced (Reaction R5) inside the pore of the char particles by heterogeneous or homogeneous reactions in the presence of CO catalyzed by char surface and inorganic components [22, 23]. During char oxidation (Reaction R4) N_2O is also formed to a much lower degree through homogeneous mechanism involving the release of HCN and HNCO (Reaction R6) and the following reaction of NH and NCO radicals with NO (Reaction R7), or through heterogeneous oxidation of the char-N (Reaction R4). The formed N_2O can be, in turn, reduced to elementary nitrogen in presence of H_2O vapor and CO (Reaction R8) [24].

4. NOx control in small scale biomass combustion

Advanced understanding of the fuel-N mechanism contributes to the development of combustion technologies with reduced NOx emissions. Several methods used in large combustion plants to control NOx emissions such as air staging, fuel staging, flue gas recirculation, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR). While the first three methods are primary measures (i.e., applied directly in the region where the fuel is burned), the latter two are secondary measures applied downstream the combustion area. The detailed description of the methods can be found in [2, 20, 25]. The application of these measures to small scale heating appliances (<35 kW) is frequently not equally efficient or feasible because of technological/operational aspects (e.g., too small combustion chambers) and excessive costs of the abatement with respect to the heating appliance cost.

Nonetheless, many authors experimentally investigated the application of some of the NOx control strategies on medium scale (35 kW – 500 kW) biomass boilers and laboratory-scale combustors. Especially the application of air staging drew attention for its relative simplicity.

4.1 Air staging applied to small heating appliances

In air staging the combustion air is introduced into the furnace in stages, creating a fuel-rich zone in the primary combustion zone where reduction conditions prevail due to lack of oxygen, and a burnout zone where more air is injected to complete the fuel combustion. Air staging applied to biomass combustion in small scale combustion appliances was studied in literature through tests on real-scale plants or in laboratory furnaces, as well as with computational fluid dynamics (CFD) studies.

Different air staging configurations have been experimented on an underfeed stoker biomass pellet boiler (50 kW) including varying primary to secondary air ratios and different heights of the secondary air inlets above the fuel bed [26]. Their results showed that air staging lead to an effective NOx reduction especially during combustion of fuels with higher fuel bound nitrogen. The height of the secondary air inlets above the bed was found to have important impacts on both NOx and CO emissions. They suggest the adoption of bigger/taller combustion chambers in the design. The lowest NOx emissions were achieved under ‘strong staging’ conditions corresponding to a stoichiometric ratio of the primary combustion zone of about 1.25, while maintaining good combustion conditions and ‘acceptable’ CO emissions. They however point out the need to carefully consider the trade-off between NOx and CO emissions since air staging may cause an increase in CO and unburnt hydrocarbons.

The parameters influencing NOx control in various techniques can be further investigated with laboratory reactors. Primary excess air ratios similar to boiler tests were found also in these studies. For example, NOx emission control by air-staging has been studied through experiments with a grate-combustion multifuel reactor fed with different pelletized biomass feedstocks and their mixtures [27, 28]. The experiments revealed that air-staging can be effectively used for the NOx emission reduction from grate biomass combustion. The primary excess air ratio was found to be the most important parameter and an optimum value of 0.9 (fuel rich condition) was defined for the experimental conditions investigated. It was observed that the optimum value may be influenced by low ash melting characteristics of the fuels if sintering occurring on the fuel grate lowers the actual available oxygen with respect to the amount fed to the reactor [28]. Experimental results for both staged and non-staged air combustion have shown that NOx emission levels are not affected significantly by temperature for temperatures lower than 1000°C [27]. A similar lack of influence for the temperature was shown burning woody biomass in a pellet boiler (35 kW) with air staging and flue gas circulation [29]. This study concluded that the optimum primary air ratio is independent of the fuel used for any given technology whereas the actual primary air ratio at which NOx emissions are minimized is a characteristic of the technology/boiler design. It was also highlighted that high NOx emissions of energy grasses can be reduced by up to 30% by air staging. Discussing the effect of residence time on NOx reduction efficiency with inherent literature data [30, 31] it is concluded that residence times greater than 0.3-0.7s are required to optimize NOx reduction and primary combustion chambers in residential heating boilers are often too small (short residence time) for efficient NOx reduction.

Regarding small wood log burning room heaters, NOx emissions from wood stoves were studied through computational fluid dynamics (CFD) modelling of a 5 kW natural draft wood log stove with primary air injected through slots at the bottom, secondary air through holes at the back wall of the stove and flushing air injected vertically through a slot above the front glass window [32, 33]. This configuration is different than the classic air staging in boilers since the mixing of fuel gas and primary air is far from complete before the secondary air is injected. The results have shown a significant NOx reduction at a primary excess air ratio of 0.8, indicating the potential of NOx reduction by staged air combustion also in these small domestic appliances. Air staging was proposed also by other authors as an efficient way of reducing emissions for chimney stoves without specific reference to NOx emissions [34].

The performance of a lambda-sensor-controlled pellet boiler (15 kW) fired with agricultural fuels was tested [35] and lambda control was discussed as an efficient way to reduce NOx emissions especially for non-woody biomass fuels without compromising complete combustion. Another study investigated the influence of excess air and air distribution on the emissions of domestic top-fed pellet stoves (12 kW) with various combustion chamber heights (i.e., base model, shorter, taller), and burner pot configurations, these latter differing in the total area, the primary air inlet area, and the ratio between the inlet area for primary and secondary air [36]. The excess air was identified as the main parameter influencing NOx emissions, with no striking effect either of pot design or of the combustion chamber height. While NOx emissions showed an increasing linear relationship with flue gas O_2 when burning wood pellets (usually fuel-N<0.1%w) [36], NOx emissions were relatively insensitive to excess oxygen in the flue gas during combustion of grass pellets or grade 3 wood pellets (fuel-N=0.19%w) [37].

The effect of air staging ratios on the burning rate and emissions of a low-scale biomass combustor with an underfeed fixed-bed (5-12 kW) was studied [38] exploring the influence of using lower air staging ratios (15%-30%) with respect to regular ratios used for commercial boilers and burners (30%-50%, [26]). It was shown that an increase in the total airflow rate generates a higher fuel devolatilization in the bed and a greater availability of air in the secondary zone to burn the volatilized matter. Increased NOx emissions corresponding to increased primary airflow suggested associations with the increase in the burning rate.

The emissions from a modern wood pellet boiler (25 kW) for residential heating was studied with different air-staging settings and under different load operations (full load, half load, minimum load) [39]. Air-staging was experimented with alternatively reduced primary (71-82% decrease) and secondary air (17-33% decrease) simultaneously keeping constant the total air/fuel ratios. No striking differences in the emissions were observed for various experimental conditions.

4.2 Alternative methods

Given the direct relationship of NOx emissions with the fuel-N content some authors have also investigated fuel pre-treatment as a way of reducing NOx emissions. For example, wood washing was experimented as a pre-treatment on beech, oak, and fir woods, all with fuel-N content lower than 0.1 %$_w$ [40]. The combustion of pelletized washed-biomass in a domestic pellet stove showed that the washing procedure did not affect the emissions of NOx in the exhaust (Fig. 2).

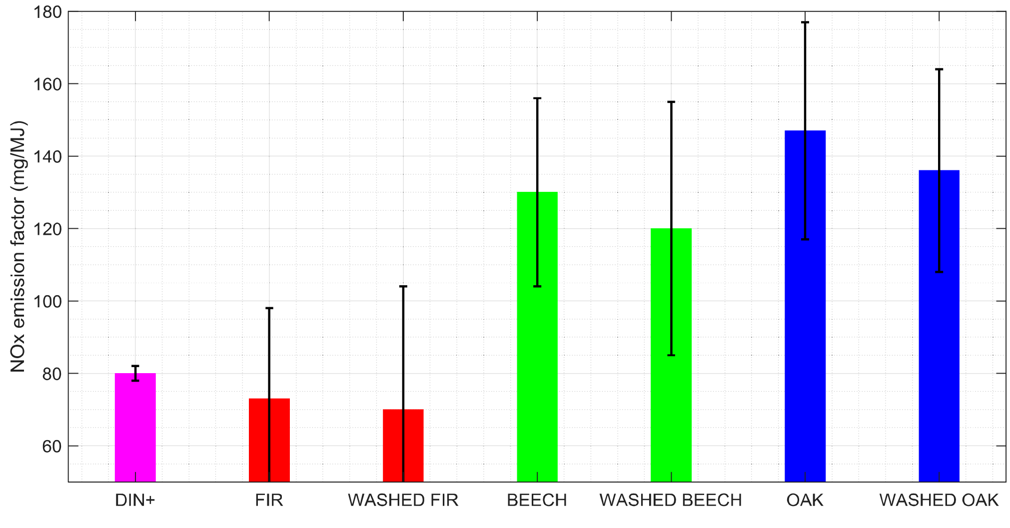

Fig. 2. Average and standard deviations of NOx emission factors from combustion of washed and non-washed biomass [40]

Another study [41] observed co-benefit in NOx reduction of fuel additives while investigating assortments to produce bench-scale agricultural biomass test fuels compliant with local boiler tests criteria. The effect of fuel additives on the emissions was tested on a pellet boiler (49 kW) with separately controllable primary and secondary air firing herbaceous biomass, namely wheat straw pellets (WSP, fuel-N=0.9%$_{daf}$) and wheat grain pellets (WGP, fuel-N=1.6%$_{daf}$) as base case. No notable difference was observed between base case WSP and test fuel with additives containing various mixtures of $KCl+CaCl_2$ (test fuel-N=0.8%$_{daf}$), or $K_2CO_3+CaCl_2$ (test fuel-N=1.3%$_{daf}$). Interestingly, the addition to WGP of some bottom ash from the combustion of the very same wheat grain assortment (test fuel-N=2.5%$_{daf}$) decreased NOx concentrations of about 23% with respect to the base case (from 505±19 mg/m^3 to 388±38 mg/m^3).

5. NOx emission factors in the literature

5.1 Influence of fuel bound nitrogen on NOx emissions

Many authors have highlighted the relationship between fuel-N and NOx emissions explained in section 3. For example, relevant combustion properties of fuels obtained from woody and herbaceous biomass, as well as some agricultural and industrial residues were studied in order to propose fuel indexes applicable to predict combustion related problems in fixed-bed biomass combustion systems [42]. Fuel-N was used as an indicator for NOx emission potential and increasing NOx concentrations were observed with increasing fuel bound nitrogen [42, 43]. This finding is congruent with many other studies on domestic biomass appliances fired with fuels with different fuel-N content [37, 44, 45, 46, 47]. An opposite trend is obtained for the conversion rate of fuel-N to N in NOx emissions which decreases for higher fuel-N content. It is concluded that for state-of-the-art grate-fired combustion units with air-staging technology burning medium- (0.4-1 %$_{w,db}$, e.g., short rotation crops, straw) to high-N fuels (1-10 %$_{w,db}$, e.g., cereals, waste wood) NOx concentrations higher than 200 mg/m^3 (NTP, dry gas, 13% O_2) are to be expected [42].

In the present study, the relationship between the fuel-N content and NOx emissions is explored based on the reviewed experimental emission factor data. Fig. 3 shows the literature NOx emission factors lumped into groups in function of the fuel bound nitrogen content. Except few data points scattered outside the ±2.7σ region, for fuel-Ns lower than 0.4%$_w$ average emission factor is about 64 mg/MJ (roughly 94 mg/m^3 NTP, 13%O2). The 75th percentile value for fuel-Ns lower than 0.8%$_w$ is 142 mg/MJ (roughly 209 mg/m^3 NTP, 13%O_2). This fuel-N range (fuel-N < 0.4%$_w$) covers most of the woody biomass frequently used in room heaters as well as some non-woody or residual biomass (e.g., wheat, walnut shell) tested in domestic boilers. Ample variability in NOx emission factors is present for fuel-Ns within the range 1.1%$_w$-2.3%$_w$ with an average value of 187 mg/MJ (roughly 275 mg/m^3) and 90th percentile of 433 mg/MJ (roughly 637 mg/m^3). Higher nitrogen content in the fuel (> 2.3 %$_w$) surely requires advanced NOx control measures since average emission factors are placed around 513 mg/MJ (roughly 755 mg/m^3) and 90th percentile of 679 mg/MJ (roughly 998 mg/m^3).

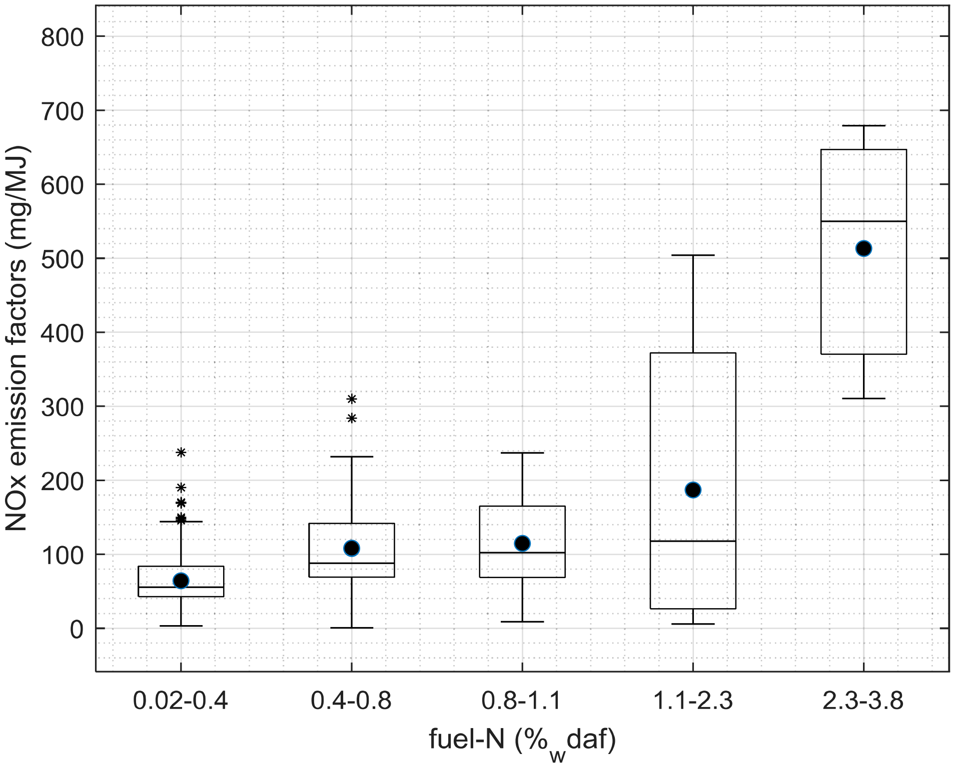

Fig. 3. Literature NOx emission factors grouped by fuel-N. (daf: dry ash free)

Regarding the conversion of fuel bound nitrogen into nitrogen in NOx emissions ($X_{NOx\text{-}N/fuel\text{-}N}$) Fig. 4 shows an exponential decline ($X_{NOx\text{-}N/fuel\text{-}N} = 1.014\ e^{-101.97\ N} + 0.1541\ e^{-0.2796\ N}$) in the conversion with increasing fuel-N, confirming the trend mentioned by [42]. The same dependency expressed in the form of a power function ($X_{NOx\text{-}N/fuel\text{-}N} = 0.08124\ N^{-0.7405}$) was very similar to observations made for industrial chip boilers (300-2500 kW) [48] and for a laboratory combustor fed with several woody/non-woody fuels and fuel mixtures [49], despite the smaller scale of the heating appliances and the greater heterogeneity of appliances, fuels and operating modes considered in the present review study. The minimum conversion potential representative of the combustion at the optimum condition (i.e., primary excess air ratio of 0.9–0.95) is also graphically of a similar in shape [28]. The reduction in the conversion rate with increasing fuel-N is explained by the promoting effect of the presence of NO on the production of N_2 because the concentration of nitrogen species in the gas phase, including NO, increases when burning high-N fuels [21].

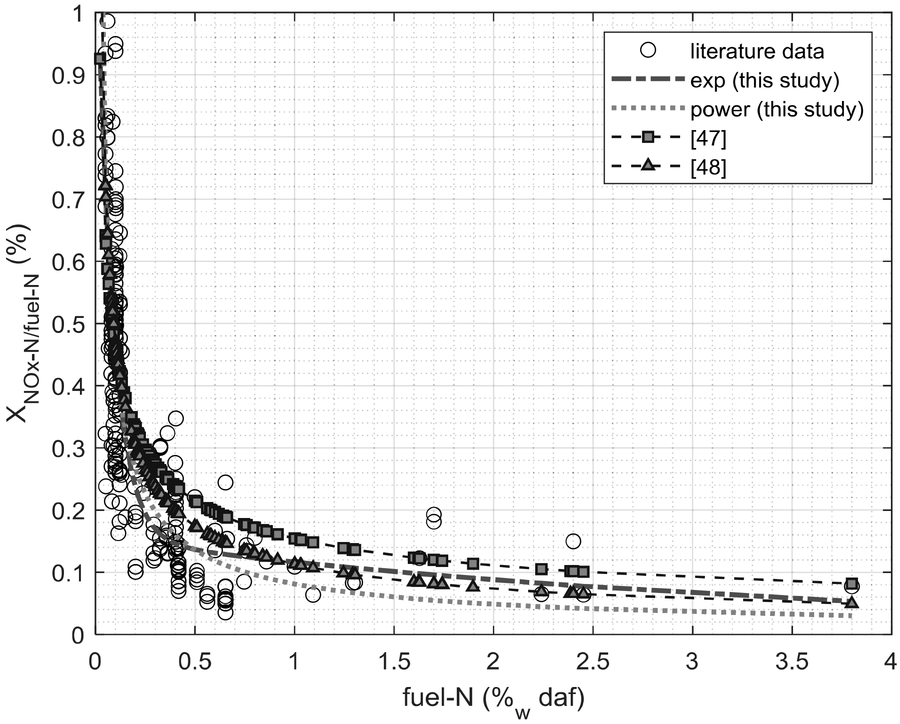

Fig. 4. Conversion of fuel bound nitrogen into nitrogen in NOx emissions ($X_{NOx\text{-}N/fuel\text{-}N}$) (daf: dry ash free)

5.2 Influence of other fuel constituents on NOx emissions

The NOx release in biomass combustion is regulated by a combined effect of fuel-N, fuel carbon (fuel-C) and fuel-ash content. As seen in Fig. 1, fuels with lower fixed carbon are expected to have lower emissions associated with char oxidation and net NOx formation from fuel-N is influenced also by char-surface catalyzed reduction reactions.

The char/ash-effect on the formation and destruction of NOx was observed during tests on a multi-fuel domestic boiler (40 kW) firing the appliance with several different woody and non-woody biomass pellets (e.g., herbaceous biomass, agriculture wastes) with fuel-Ns ranging from 0.4%w for wood pellets to 1.7%w for food industry residues [9, 50]. Distinct behavior in NOx emissions was observed for different type of pellets and the importance of considering the catalytic effects of char and ash on the formation and reduction of NOx was highlighted when dealing with high-ash fuels such as agro-pellets. The authors report a 7-fold increase in NOx emissions for straw pellets (fuel-ash=10.7%$_w$, fuel-N=0.9%$_w$) with respect to wood pellets (fuel-ash=0.41%$_w$, fuel-N=0.1%$_w$). Ref. [18] discuss that most solid biofuels obtained from agricultural residual biomass have high contents of volatile matter and low contents of fixed carbon with reduced effect of char on the formation of NOx, nonetheless the catalytic effect of the ash could be important for some residual biomass such as cotton husks, mustard husk, soya husks and groundnut husks which have high CaO contents that can lead to active surfaces capable of catalyzing the reduction of NO and N_2O.

Higher amounts of carbon is reported [51] to correspond to a higher net conversion of fuel-N to NO because as the carbon content increases, nitrogen is preferably bound in heterocyclic structures leading to the formation of HCN, rather than being present in the form of amines or quaternary-N structures, leading to the formation of NH_3 which is a stronger reductant of NO than HCN. This latter on the other hand tends to reduce NO to N_2O, rather than to N_2, and N_2O can degrade again to NO in fuel lean conditions and at low temperature.

5.3 Influence of appliance type and operating conditions

41 scientific papers [6, 7, 9, 39, 41, 47, 50, 52-69,71-86] were consulted in order to give an overview of NOx emission factors from small scale biomass combustion appliances (Table 1). The highest NOx emission factors were observed for automatic boilers and stoves burning non-woody biomass (average: 286 mg/MJ; 95%CI: 224 mg/MJ-398 mg/MJ) and the lowest for manually fed stoves and boilers burning firewood (average: 67 mg/MJ; 95%CI: 63 mg/MJ-72 mg/MJ). Feeding the automatic appliances with woody biomass and the usage of non-woody biomass in manually fed appliances give comparable emissions factors with an average of 79 mg/MJ (95%CI: 74 mg/MJ-86 mg/MJ) for the former and 98 mg/MJ (95%CI: 50 mg/MJ-180 mg/MJ).

Varying operating conditions and transitory periods have been shown to have a limited effect on NOx emissions for automatic boilers. For example, tests on a domestic wood pellet boiler (22 kW) have shown that NOx emissions have a marginal dependence of the boiler operating conditions (excess air range around 2.6-4.6) [44]. Comparable emission factors for the steady operation and transitory periods were obtained testing the emissions of residential combined solar-wood pellet heating systems (12-20) under a realistic operation sequence including start-up and stop phases [55]. Reducing the number of start and stops by modulating the appliance power and using buffer stores had no visible effect on NOx emissions. Since NOx release depends strictly on the fuel bound nitrogen, hence the fuel consumption, the start and stop phases accounted only for the 10%-20% of accumulated NOx emissions throughout the operating sequence. A lack of marked differences between low to high power operation was also obtained during tests on 12 kW – 20 kW boilers and a stove fired with woody pellets [56]. Tests on a top-feed wood pellet boiler (25 kW) with controlled secondary air have shown that average NOx emission factors were almost equal for the boiler start phase and the optimal operating conditions [57]. The optimal operation entailed only less variability in the data. Reduced secondary air and the associated reduced oxygen supply slightly decreased (about 10%) the emission factors. Similar observations were made on further studies on the same boiler [58]. However, switching to a fuel with twice as much fuel-N almost doubled the emission factor for the same boiler operating under optimal conditions stressing the importance of fuel-N mechanism on NOx formation [57]. Slightly decreased NOx emission factors (about 15%) were observed by closing the secondary combustion air inlet of a two-stage up-draft pellet boiler [59]. Tests on 3 room heaters fed manually with different woody biomass has shown that inclusion in the simulated real-life combustion cycles of final batches with limited combustion air supply did not have a significant effect on NOx emissions [60].

The influence of operating conditions seems to be more marked for automatic room heaters with respect to boilers. In fact, for wood pellet stoves operated under full load an increase of about 30%-35% in the emission factor was observed with respect to the operation under partial load [59, 61]. An even higher emission factor was observed during operation with higher burn rate (1.4-fold increase with respect to nominal load) [61]. Other tests with woody biomass on a pellet stove (6 kW) and a multi-fuel chip boiler (40 kW) indicated higher influence of the full load operation with respect to partial load operation when testing the wood chip boiler rather than the pellet stove [62]. Limited effects of stove load on NOx emission factors between high and low loads were also reported for other stoves [63]; only a small a decrease (around 10%) in NOx emissions under low load conditions were noted with lower excess oxygen in one of the tested stoves.

The user behavior influence (i.e., fuel charging, combustion air control, fuel quality) and burning cycle (standard vs. real-life) shown to be of crucial importance for incomplete combustion product emissions such as particulate matter from manually fed room heaters results to have limited effect on NOx emissions. Ref.60 compared real-life and standard burning cycles (EN 13240:2001) and observed only about a 40% increase as a consequence of the non-optimal operating conditions on NOx emissions. No differences in NOx emission factors were observed between good operational practice and non-optimal operation (i.e., restricted combustion air supply and slight overload of the firebox) of a conventional masonry heater (no staged-air, only minor window flush air) [64]. Similarly, the results of the maloperation tests (i.e., minimum air level and high fuel load) on a logwood stove with secondary air inlet (6 kW) have shown no striking differences with the standard operation, interestingly the same tests on a conventional 6.5 kW stove (only primary air) caused a 30%-40% decrease in NOx concentrations during maloperation [61]. Slow ignition of a modern masonry heater equipped with air staging technology did not show any particular effect on NOx emission factors [65].

With regard to combustion phases, some authors reported higher emission factors for the flaming phase with respect to ignition and smoldering phases [59, 66] this is consistent with the fuel bound nitrogen release mechanisms reviewed previously, since during smoldering the dominant feature is the char-N conversion [67] with less NOx formation with respect to volatile-fuel-N conversion pathway.

Regarding the fuel quality, investigation of the influence of using fuels with relatively high moisture content in manually fed appliances has pointed out that similar emission factors were obtained both feeding dry (16.4% $_w$ moisture) and wet (23.5%$_w$ moisture) wood logs to a conventional single-stage logwood stove (6 kW), except for a 3-fold increase during the burn-out phase of one of the wet-log tests [59]. The same authors report about a 30% decrease in the flaming phase emission factor when using wet logs (42.4%$_w$ moisture) instead of dry logs (13.3 %$_w$ moisture) in a two-stage batch operated downdraft automatic wood boiler. The emission performance of a residential stove (5.7 kW) burning high moisture woody biomass was studied and it was concluded that NOx emissions were more affected by the fuel-N content rather than the fuel moisture [68]. Nonetheless, the study suggested that for the tested hard wood species the fuel moisture may influence the nature of the emission of the nitrogen species (i.e., partitioning between NOx and NH_3). On the contrary, increased emission factors were observed in another research study on the combustion of wet branches in a wood stove (30 kW) for domestic hot water and space heating [69]. Similar findings were obtained on a domestic heating wood chip boiler (50 kW) fed with logs of the same wood type but with different moisture levels (<25%, 26-39%, >40%) with almost tripling concentrations for the moist fuel (>40%) during the full load operation [70]. Moisture is reported to potentially affect the quality of the combustion by greatly delaying the release of the volatiles [18].

5.4 Comparison with fossil fuel alternatives

The comparison of the literature residential heating experimental emission factors for biomass combustion and common fossil fuels is shown in Fig. 5. Average emission factor for automatic biomass appliances fed with woody biomass (79 mg/MJ) is1.3 times the average emission factor reported for light oil boilers (61 mg/MJ) under various operating conditions

[47, 52, 53, 54]. About a two-fold increase is observed when compared with the natural gas boilers (41 mg/MJ) studied in literature [53, 54].

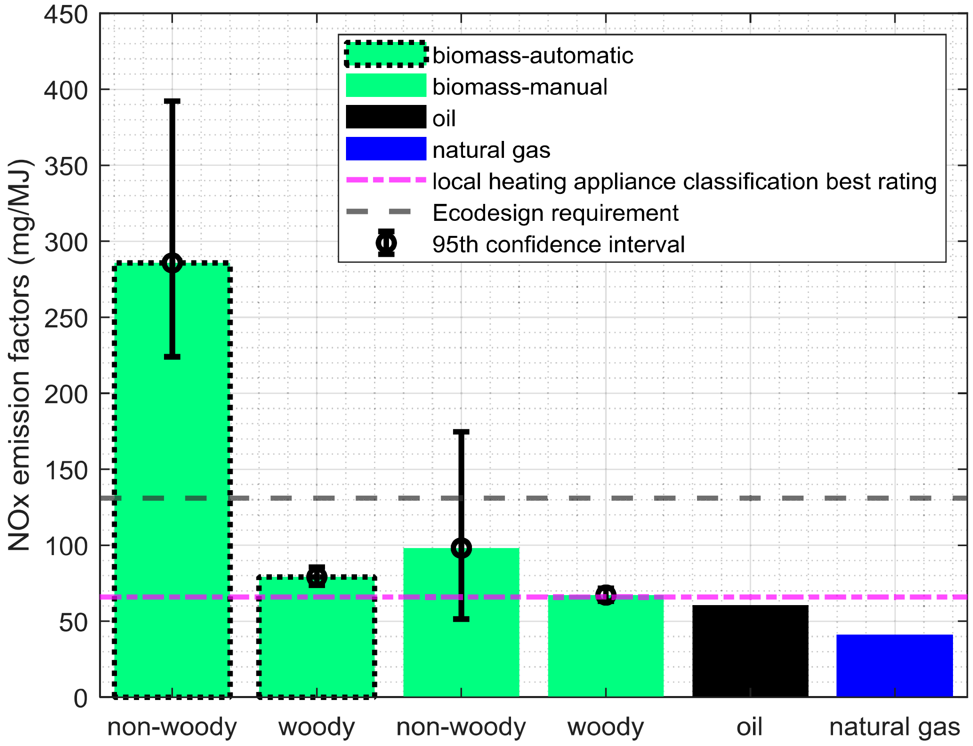

Fig. 5. Comparison of experimental emission factors for biomass and fossil fuels (grey and magenta dashed lines indicate the regulatory standards)

5.5 Regulatory frame implications

Source-specific emission standards are set within EU Clean Air Policy Framework to reduce the emissions from domestic combustion. Eco-design Directive through the Commission Regulations (EU) 2015/1185 and (EU) 2015/1189 provide minimum requirements to this effect, and state that, mandatory from 2020 (1^{st} January 2022 for local space heaters), emissions of NOx by biomass burning local space heaters and boilers shall not exceed 200 mg/m3$_{@13\%O2}$ (roughly 131 mg/MJ). Some local authorities take a further step and introduce appliance classifications to regulate the market introduction and use of biomass heating appliances to contrast the air quality problems related to this emission source. One such example is the Italian Decree n. 186 (2017) which establishes since 2018 the requirements, procedures and competences for the environmental certifications of heat generators fed with firewood, charcoal and biomass fuels. This decree introduces a limit of 100 mg/m3$_{@13\%O2}$ (roughly 66 mg/MJ) for best performing appliances.

Considering that most of the collected NOx emission factors refer to literature data of the last ten years, the appliances are inclusive of relatively newer and older installations that would reflect many territorial realities where the gradual replacement of the stock of appliances by cleaner ones is still ongoing. The comparison of these emission factors (Fig. 5) with the appliance classification in the above-mentioned Decree n.186 points out that the wood burning stoves and boilers though complying with Eco-design requirements are placed at the limit if not below the best rating. On the other hand, none of the reviewed automatic boilers burning non-woody biomass is compliant with Eco-design requirements indicating hard times for the introduction in the market of alternative solid biofuels. Research conducted to this end [87] though giving hopeful results for the fulfilling of the emission limits of other pollutants, points out that the utilization of primary measures would not be enough to reduce the high NOx emissions below the respective emission limit for many solid biofuels investigated.

6. Conclusions

The main aspects regarding the NOx emissions from biomass combustion in domestic heat production can be synthesized as:

- NOx formation in biomass combustion is dominated by the fuel bound nitrogen (fuel-N). mechanism, hence, the main parameter that influences the emissions is the fuel-N content. However, the fuel composition in terms of ash, volatile matter and fixed carbon content will also affect the transformation of the released N-species. The conversion of fuel-N to the nitrogen in NOx emissions is not linear: the conversion rate decreases exponentially with increasing fuel-N.

- Consistent with the fuel-N mechanism especially non-woody biomass utilization should be accompanied by proper abatement measures given the usually high fuel-N content in these biomasses.

- The control of NOx emissions from residential biomass combustion however is not straightforward as the available control techniques are not feasible or less efficient when applied to small systems due to technological/operational aspects and excessive costs of the abatement with respect to the heating appliance cost.

- Air-staging strategy is widely used to control NOx emissions however its application to small appliances should carefully consider the trade-off between NOx and CO emissions since air staging may cause an increase in CO and unburnt hydrocarbons.

- Operational parameters for NOx emission control are the excess air ratio, and the distribution of primary and secondary air, residence time and temperature. Some authors conclude that the optimum primary air ratio is independent of the fuel used for any given technology whereas the actual primary air ratio minimizing NOx emissions is a characteristic of the technology/boiler design. Residence times required to optimize NOx reduction are hardly achieved in small scale appliances as the combustion chambers are frequently too small (short residence time). The effect of temperature is reported to be limited for temperatures lower than 1000°C.

- Biomass combustion systems emit relatively high levels of PM and NOx with respect to the combustion systems of light fuel oil or natural gas. Nevertheless, the comparison of environmental performance of the appliances should not be limited to the emission factors but a more complete analysis (cradle to grave) should be performed with the aid of for example life cycle analysis methodology, which may surface aspects not directly related to stack emissions.

The present review study highlighted the need to conduct further research on NOx abatement technologies in small scale heating appliances. Since the use of alternative solid biofuels with higher fuel bound nitrogen such as residual biomass (e.g., agricultural, industrial residues) for heat production may potentially cover a strategic role in circular economy it is fundamental to develop after-treatment equipment (i.e., secondary removal measures) also for domestic heat production appliances. Expanding to centralized heating (district heating) where the relatively larger scale of the appliances helps to overcome the techno-economical barrier in the application of both primary and secondary NOx control, may also be an option to reduce the emissions related to this emission source.

7. References

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Figure1

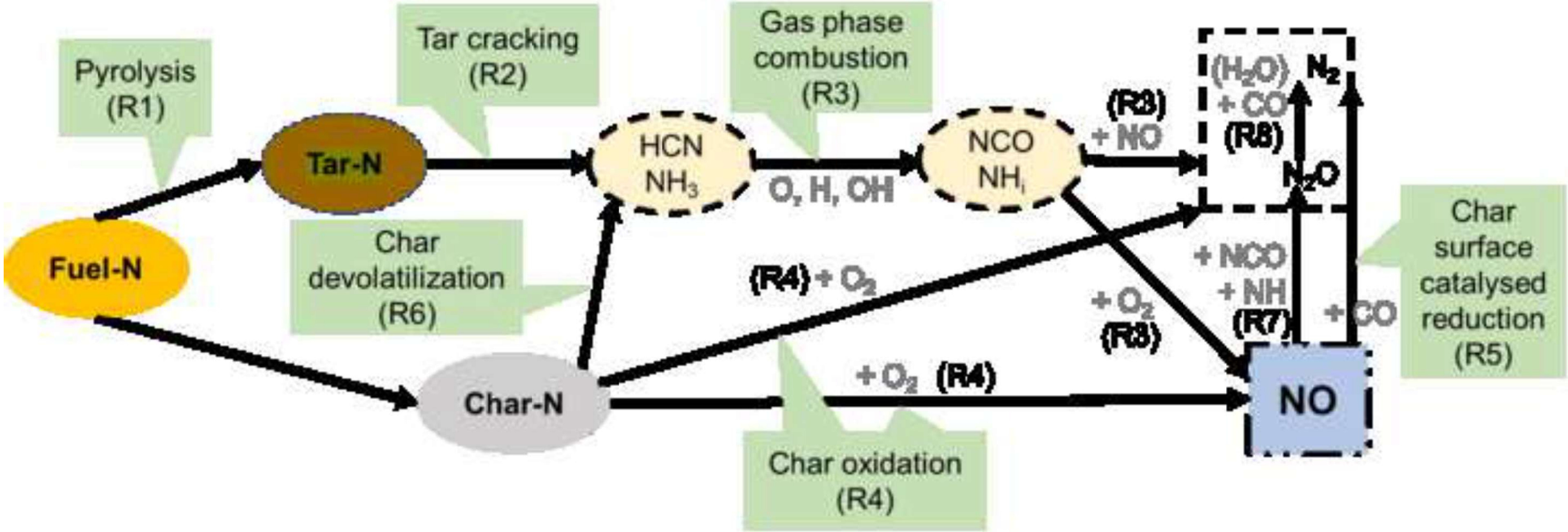
Pyrolysis (R1)
Tar cracking (R2)
Gas phase combustion (R3)
Fuel-N
Tar-N
HCN NH_3
O_2 H, OH
NCO NH_i
(R3) + NO
(H_2O) + CO (R8)
N_2
N_2O
Char devolatilization (R6)
(R4) + O_2
+ O_2 (R3)
+ NCO + NH (R7)
+ CO
Char surface catalysed reduction (R5)
Char-N
+ O_2 (R4)
NO
Char oxidation (R4)

Figure 2

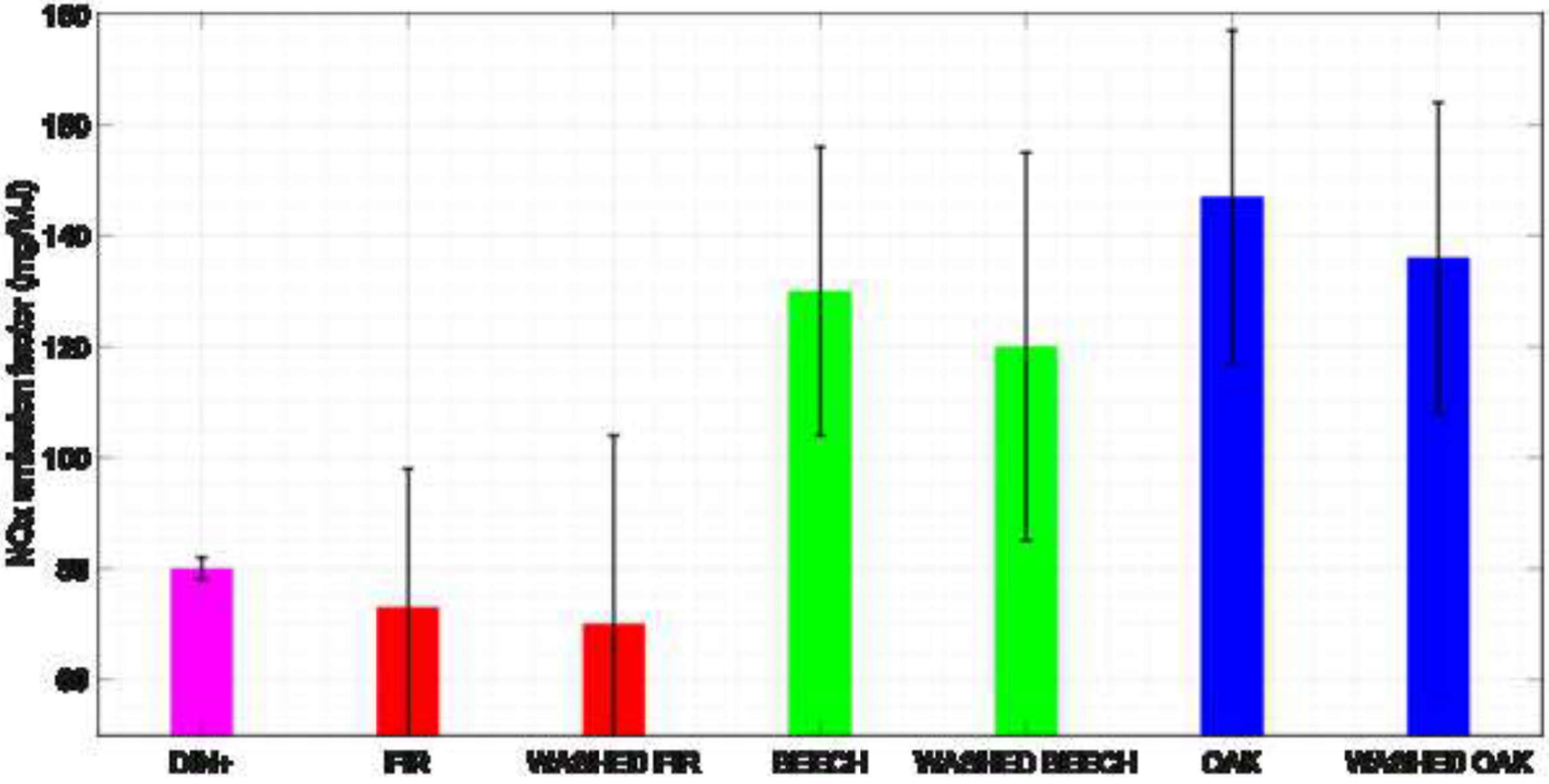
NOx emission factor (mg/MJ)
180
160
140
120
100
80
60
DIN+
FIR
WASHED FIR
BEECH
WASHED BEECH
OAK
WASHED OAK

Figure 3

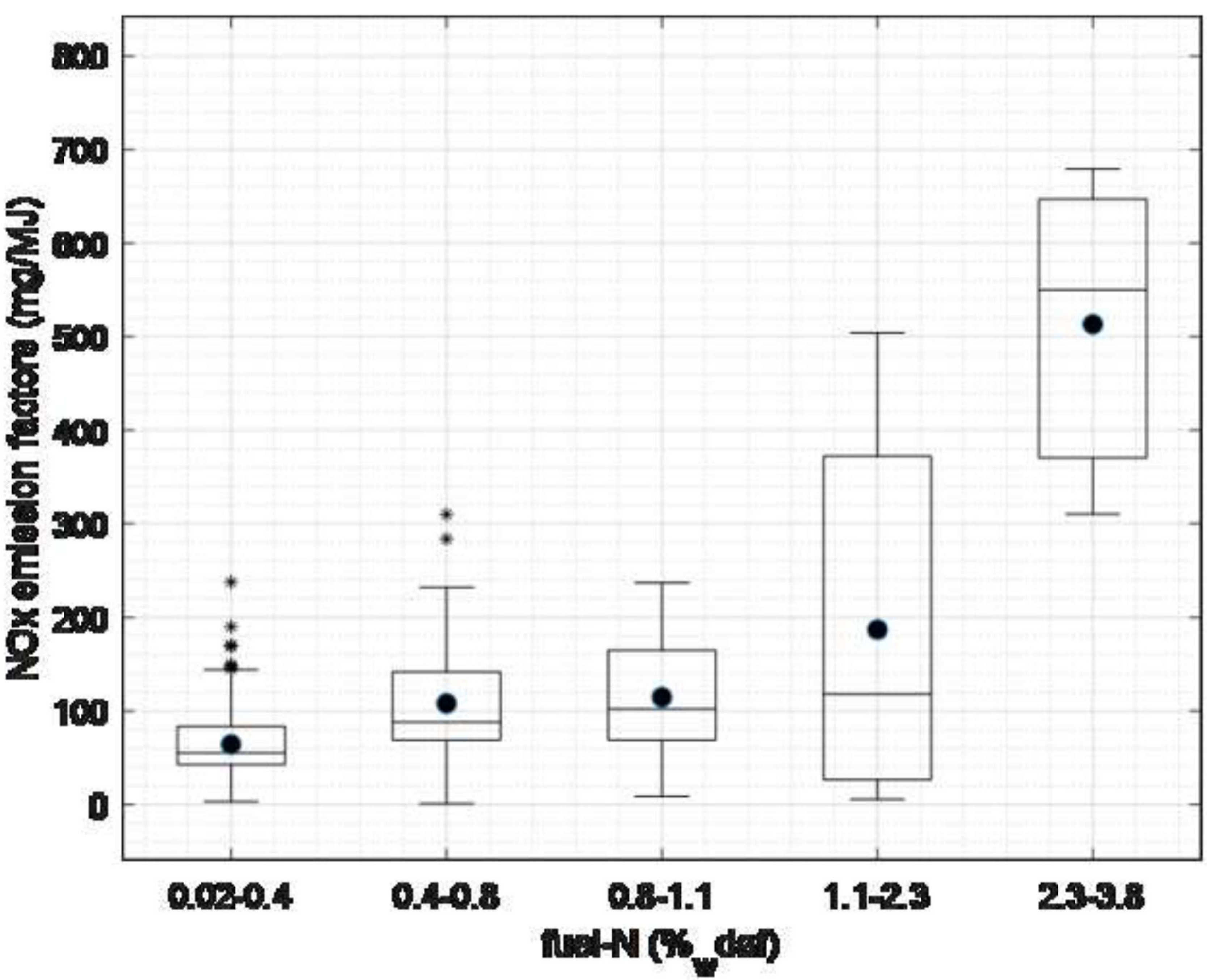
NOx emission factors (mg/MJ)
800
700
600
500
400
300
200
100
0
0.02-0.4
0.4-0.8
0.8-1.1
1.1-2.3
2.3-3.8
fuel-N (%$_w$ daf)

Figure 4

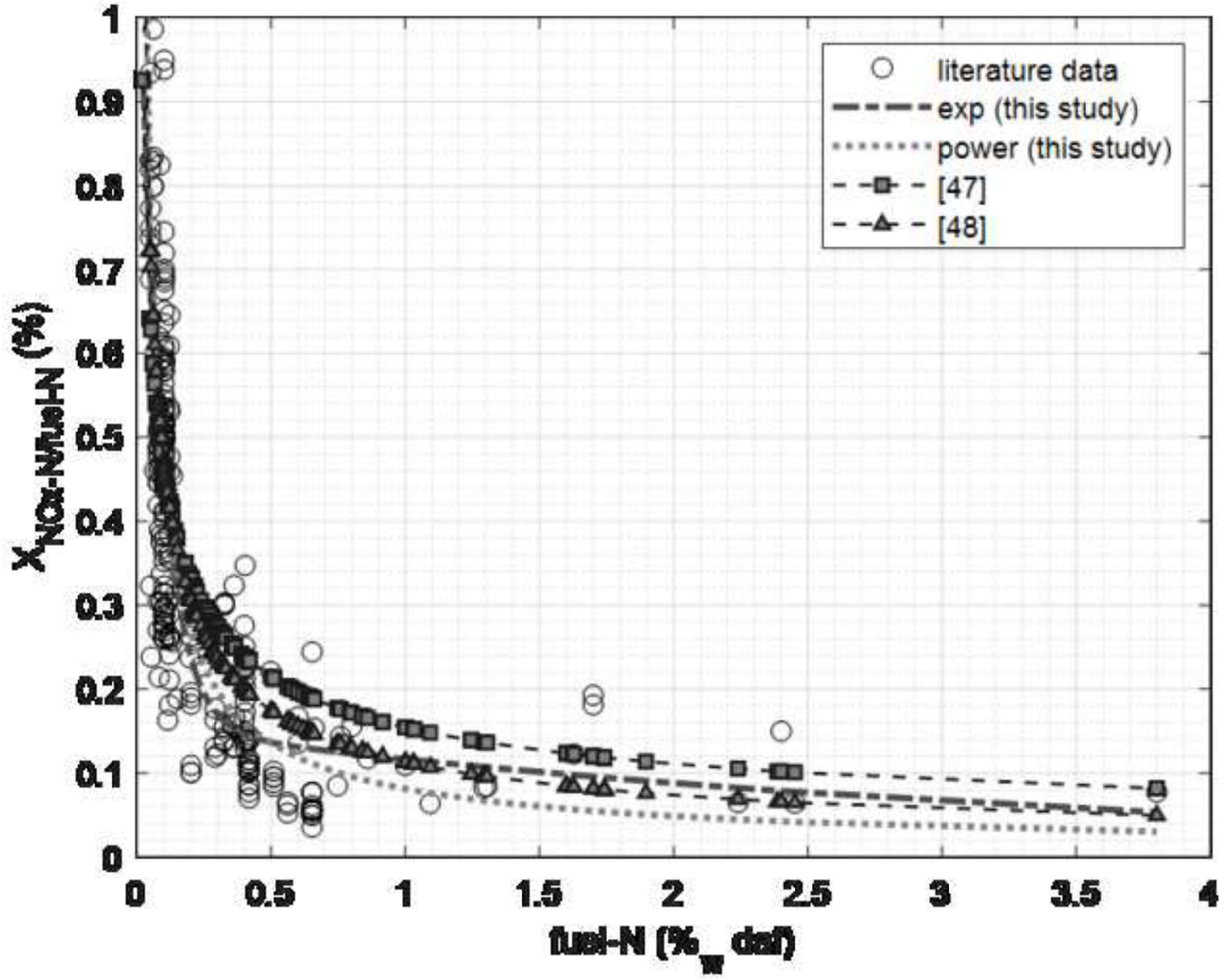
literature data
exp (this study)
power (this study)
[47]
[48]
$X_{NOx\text{-}N/fuel\text{-}N}$ (%)
fuel-N ($\%_w$ daf)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
0.5
1
1.5
2
2.5
3
3.5
4

Figure 5

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