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An evaluation of effects of operational parameters on NOx emissions through detailed chemical kinetics simulations

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Abstract

NOx emissions from biomass and Municipal Solid Waste (MSW) combustion is a great concern. Technologies for reducing NOx emissions based on flue gas cleaning using e.g. Selective Non-Catalytic Reduction (SNCR) or Selective Catalytic Reduction (SCR) are well known. However, limiting NOx emissions by primary measures is an attractive opportunity, avoiding or limiting the use of costly secondary measures. Many factors influence the NOx emission level from biomass and MSW combustion plants, like fuel-N content and speciation, and operating parameters as air distribution and staging, flue gas recirculation, temperature and residence time. In this work a recent detailed chemical kinetics mechanism is used to investigate the NOx reduction potential by staged air combustion at different operational conditions, using two ideal plug flow reactors connected in series. This enables revealing a kinetics limited reduction potential, as a guideline for further detailed studies at targeted conditions using stochastic reactor networks or Computational Fluid Dynamics (CFD). The results show, for demolition wood as fuel, a large NOx reduction potential, as high as above 95% total fixed nitrogen reduction at theoretically optimum conditions. Through reaction path analyses the main reaction pathways and reactions are identified. Comparison with experimental results from grate combustion units is made. Finally, a comparison with earlier and less extensive detailed chemical kinetics mechanisms is made, to check for significant differences and assess the reasons for those. The final goal would be to arrive at computationally effective reduced chemical kinetics mechanisms that could be applied in CFD simulations of real biomass and MSW combustion plants, to arrive at improved operational conditions or improved design.

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1. Introduction

NOx emissions from biomass and MSW combustion is a great concern. Increasingly stricter emission regulations and costly secondary measures motivates the use and optimisation of primary measures, such as staged air combustion. Previous work has investigated the NOx reduction potential by staged air combustion, both through detailed chemical kinetics modelling in ideal reactors [1,2], CFD simulations [3,4] and experimental work on biomass [5,6,7,8,9,10] and waste [11,12,13,14].

A wide range of NOx reduction degrees has been found, depending on both fuel properties and process conditions. For many plants applying staged air combustion, the implemented process conditions might be far away from the optimum conditions. The ideal situation would be to be able to efficiently and correctly simulate a real plant using CFD, however, as of today this is too computationally expensive as an engineering tool, as well as necessary sub-models, especially connected to the fuel, still needs to mature. Exhaustive experimental campaigns are also very expensive, especially at a plant scale.

It is therefore very interesting to use, as in this work, simulation tools to investigate kinetics limited optimum conditions for NOx reduction, revealing the influence of fuel and process conditions. This innovative knowledge can be further used to well reduce the, for CFD simulations, computationally expensive comprehensive state-of-the-art detailed chemical kinetics, to a degree still suitable for investigating the NOx reduction degree in a real plant, through CFD.

2. Methods

The software LOGEresearch [15] has been used for the simulations and kinetics analysis, using the plug flow reactor module in combination with the detailed chemical kinetics mechanism of Glarborg et al. [16]. LOGEresearch allows for 0-D homogeneous as well as stochastic reactors and has built-in options for mechanism analysis as well as reduction.

The Glarborg et al. mechanism (hereafter called PG18) is a comprehensive (148 species and 2760 reactions) and up-to-date mechanism including CHO chemistry (based on CH_4 and hydrocarbons up to C_2H_6) and nitrogen chemistry, updated to the current level of knowledge regarding species, reactions, rate constants and thermochemistry. PG18 is in this work compared to an earlier detailed mechanism (hereafter called PG13) including 81 species and 1401 reactions, also based on CH_4 and hydrocarbons up to C_2H_6. PG13 was used as a master mechanism for making reduced mechanisms suitable for use in CFD simulations of biomass combustion [17].

In that work a fuel gas composition representing demolition wood (with a fuel-N content of 1.06 wt% on dry ash free basis) was used, and this was adopted also in the current work. The fuel-N level in the fuel gas was set according to the fuel-N content, distributed on NH_3, HCN (HCN/NH_3 ratio of 0.65) and a small amount of NO (5 % of the fuel-N content). The pressure was set to atmospheric.

3. Results and discussions

Initially PG18 was compared to the earlier mechanism, PG13, and rather significant differences were found at conditions which should be relevant for achieving high NOx reduction by staged air combustion: a primary excess air ratio (L) of 0.8 and temperatures up to 1073 K, see Fig. 1. Hence, this motivates an investigation into 1) the kinetics limited optimum conditions for NOx reduction by staged air combustion and 2) identifying the main kinetics involved.

As can be seen in Fig. 1, a temperature of 873 K is too low, as a too long residence time is required to reach a significant total fixed nitrogen (TFN, total mass of nitrogen in NH_3, HCN, NO, NO_2 and N_2O) reduction, while at 973 K, 1 s residence time is sufficient, and it is as well the optimum TFN reduction temperature for both mechanisms at a primary excess air ratio of 0.8.

To investigate the influence of primary excess air ratio, PG18 was used in the further work investigating the TFN reduction at primary excess air ratios of 0.6, 0.7, 0.8, 0.9, 0.99, 1.01, 1.2 and 1.6, at the five same temperatures.
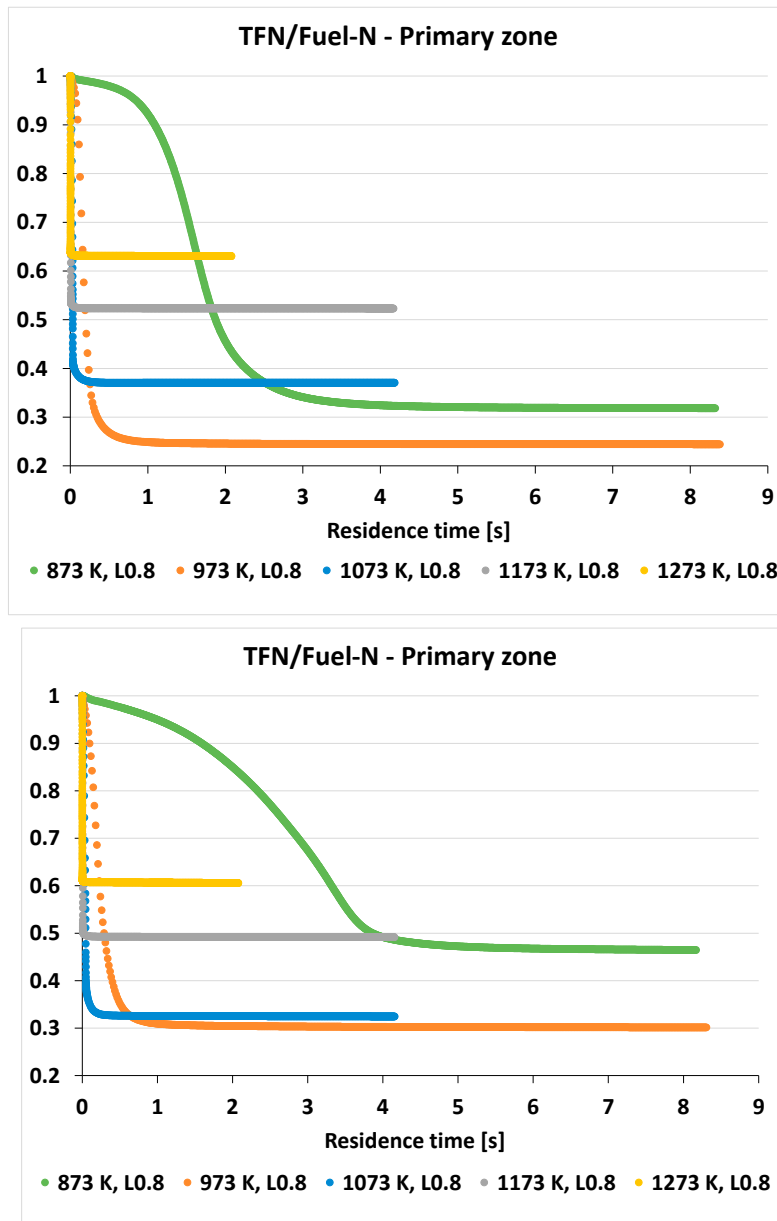

Fig. 1. Primary zone TFN/Fuel-N for PG13 (left) and PG18 (right).

Fig. 2 shows TFN/Fuel-N for all the primary excess air ratio and temperature combinations at a residence time of 1 s, dividing the TFN also into the 5 fixed N species. In general, a primary excess air ratio close to one and above 0.8 has the highest TFN reduction potential, and it is as well beneficial to keep an overall excess air ratio low (1.2 vs 1.6). However, only looking at TFN/Fuel-N is maybe not sufficient, as there also will be a further TFN reduction when adding the secondary air, even though a smaller one.

As such, as hardly no NH_3 remains, TFN in HCN represents the further NOx reduction potential, while rather limited reduction of the NO can be expected. Also, TFN in NO_2 and especially N_2O is present in significant amounts

at some conditions. The formation of N_2O is especially significant at primary excess air ratios of close to stoichiometric at moderate temperatures. This N_2O formation leaves the primary excess air ratios of 0.8 and 0.9 at temperatures of 973 and 1073 K as best for TFN reduction in the primary combustion zone. Of these, a primary excess air ratio of 0.9 at a temperature of 973 K gives the highest TFN reduction, and has the highest further NOx reduction potential through a high HCN contribution to the remaining TFN/Fuel-N.

When extending the residence time to 2 s, no significant further TFN reduction is achieved, and no change in the ranking of the best TFN reduction scenarios occur.

If the temperature in the secondary combustion zone is significantly higher than in the primary combustion zone, as usually is the case, thermal dissociation of most of the N_2O can be expected, and then also primary excess air ratios of close to unity would give a high TFN reduction at the optimum secondary combustion zone temperature.

However, keeping the temperature in the primary combustion zone low at a primary excess air ratio close to unity might be a practical challenge. The use of under-grate flue gas recirculation (FGR) would help in achieving this.
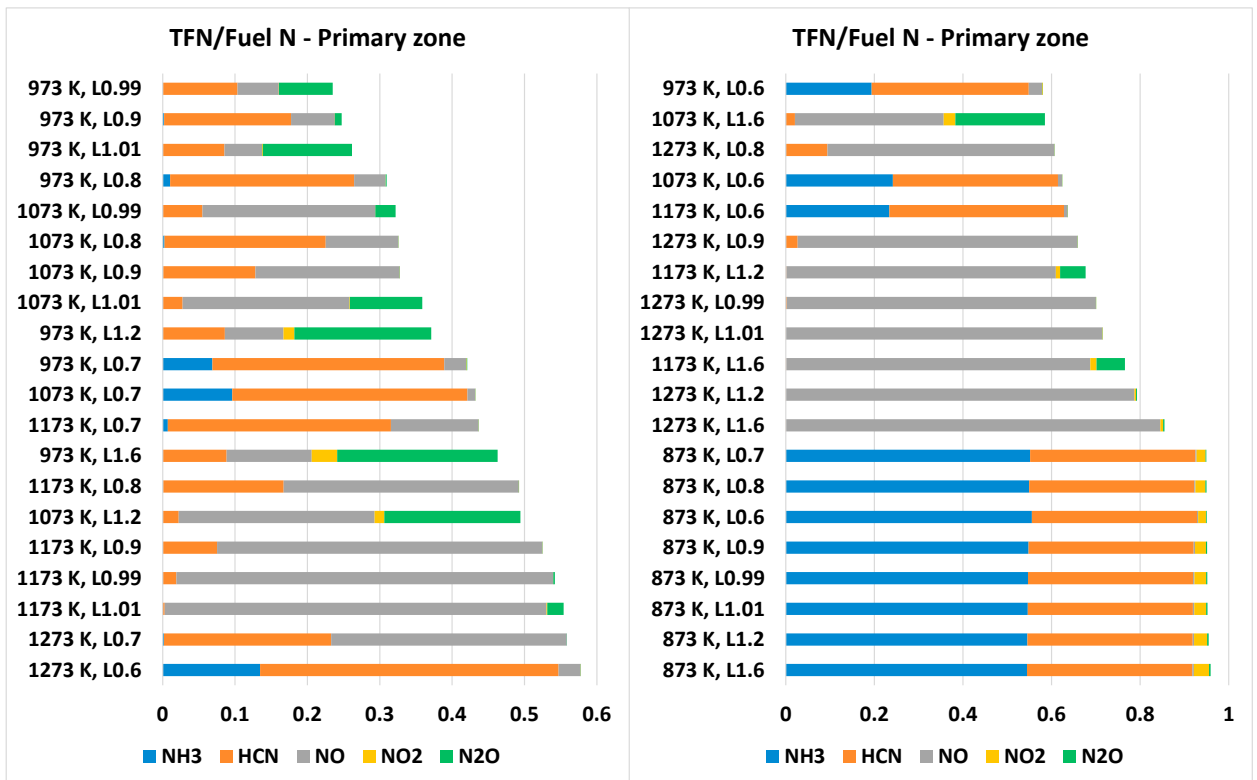

Fig. 2. Primary zone TFN/Fuel-N for PG18. Residence time: 1 s

To assess the overall NOx reduction potential by staged air combustion, the most promising combinations of primary excess air ratio (0.8, 0.9, 0.99, 1.01) and temperature (973 and 1073 K) were selected, applying an overall excess air ratio of 1.6 at a secondary combustion zone residence time of 1 s, at temperatures of equal to the primary combustion zone temperature and up to 1273 K (1473 K for a primary excess air ratio of 1.01) with 100 K intervals. The use of FGR would help in achieving lower secondary combustion zone temperatures.

Fig. 3 shows both the secondary zone and the total TFN/Fuel-N, dividing the TFN also into the 5 fixed N species. As expected, actually a very high TFN reduction is possible at a primary excess air ratio of 1.01 and a secondary combustion zone temperature of 1273 K, due to the thermal dissociation of N_2O, forming N_2.

At higher temperatures increasingly more NO will be formed from the HCN part of the TFN. If not taking the N_2O reduction potential into account and defining a primary excess air ratio of close to unity at relatively low temperature as challenging, a primary excess air ratio of 0.8-0.9 at 973 K seems like the best alternative.
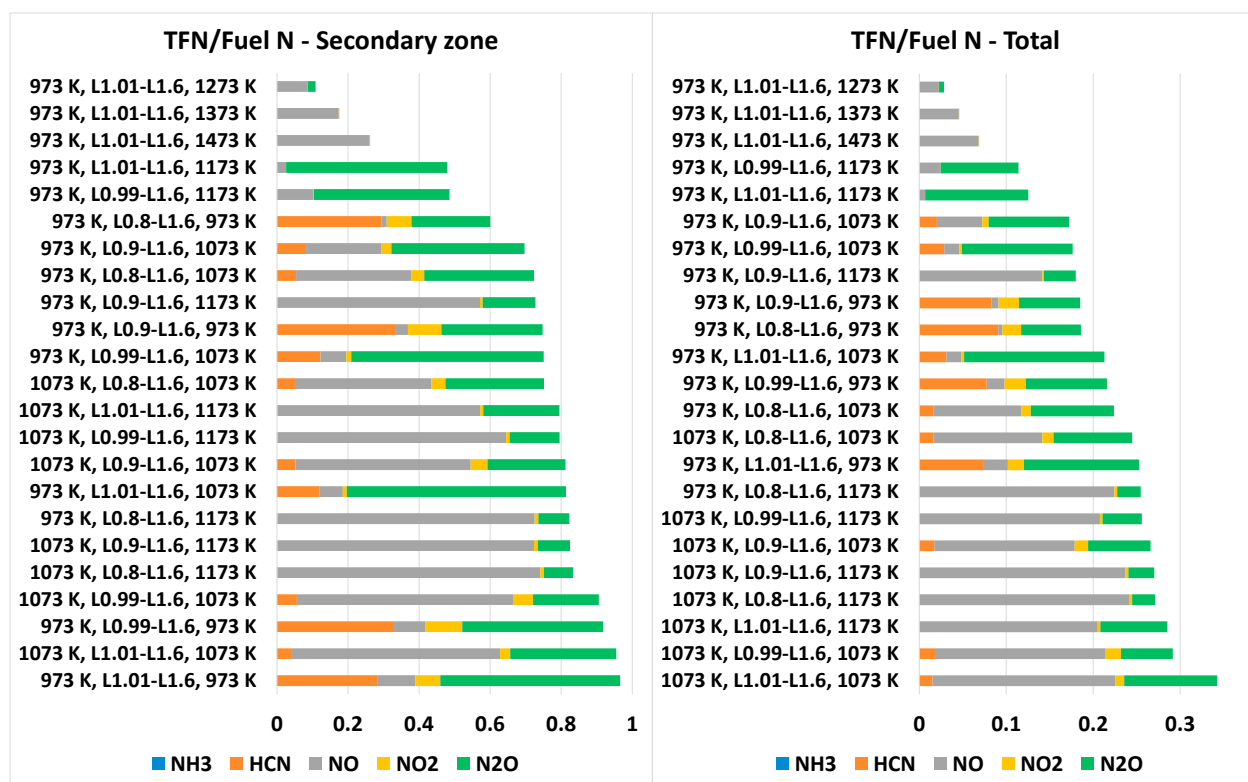
Fig. 3. Secondary zone and total TFN/Fuel-N for PG18. Residence time: 1 s, 2 s total

Reaction path analysis was carried out to assess the main conversion paths for NH_3 and HCN, to N_2 and NO, at the selected conditions, visualized for the N_2 production from N-intermediates in Fig. 4 (left) for the primary combustion zone conditions of 0.9-973 K and in Fig. 4 (right) for the corresponding secondary combustion zone conditions of 1.6-1173 K.

The reaction path analysis clearly reveals the reason for the effective NH_3 reduction in the primary combustion zone at moderate temperatures, and the reason for the need for a higher temperature for effective HCN reduction. The phenomenological behavior at 973 K is that mainly NH_3 is slowly reduced as the CHO chemistry progresses, through reaction with mainly OH and to a much lesser extent O, forming NH_2, which mainly reacts further to N_2 by reaction with NO and partly to NO via H_2NO, followed by HNO.

When the O_2 has been consumed, the CHO chemistry halts, resulting in a radical pool peak that accelerates the N chemistry, including a peak NH_3 reduction and the main HCN reduction through reaction with mainly O, forming NCO, which reacts further to mainly N_2O by reaction with NO, where after N_2O is partly reduced to N_2 by thermal dissociation and reaction with mainly H. However, at moderate temperatures the O radical pool is too small and becomes depleted too fast to achieve a complete HCN reduction.

The NO level increases steadily alongside the NH_3 reduction, as the formation of NO is larger than the reduction of the formed NO through mainly reaction with NH_2. When reaching the time of the radical pool peak, also a smaller peak NO production results, originating from both reduced NH_3 and HCN.

At higher temperatures the HCN reduction increases due to an increased O radical availability, however, also a greater fraction of the initial fuel-N is converted to NO, reducing TFN/Fuel-N. The reason for this is also more H radicals available for the nitrogen chemistry as the CHO chemistry speeds up.

As a result, a higher amount of N in the NCO formed from HCN is sourced through the reaction path NCO + H > NH + CO, NH + H > N + H_2, N + OH > **NO** + H, while a higher amount of the NH_2 formed from NH_3 is sourced

through the reaction paths $NH_2 + H > NH + H_2$, to finally **NO** and $NH_2 + O > HNO + H$, $HNO + H > $ **NO** $ + H_2$. Hence, an increase in NO formation from both NH_3 and HCN.

In the secondary combustion zone the kinetics becomes simpler, and remaining HCN will, if the temperature and residence time is sufficient, be converted to partly NO, N_2O and N_2. At sufficiently high temperatures, if having a primary excess ratio significantly below unity, N_2O will primarily be reduced fast by reaction with H, forming N_2, or a much slower thermal dissociation of the N_2O will prevail if there is a lack of H radicals. Hence, sufficient residence time is then important.

The fraction of HCN forming NO increases with increasing temperature, due to a shift in the chemistry, now favoring NCO consumption into NO ($NCO + O > NO + CO$) instead of N_2O. However, both NCO and NO is partly reduced to N_2 through $NCO + NO > N_2 + CO_2$.
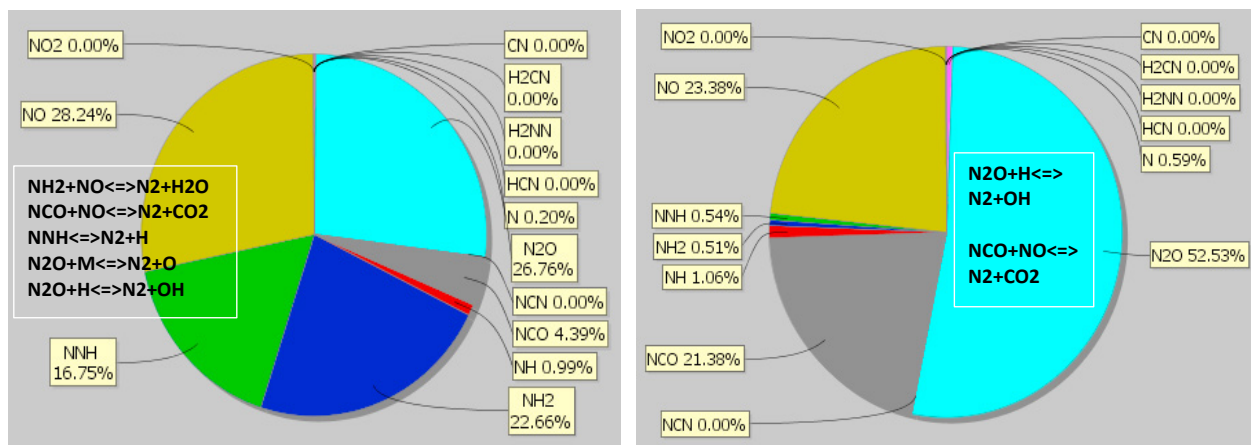

Fig. 4. Reaction path analysis showing N_2 production from N-intermediates and the main reactions for the primary combustion zone (left, primary excess air ratio: 0.9, temperature: 973 K) and the secondary combustion zone (right, overall excess air ratio: 1.6, temperature: 1173 K).

When comparing with available experimental results for the specific demolition wood also applied in this kinetics study [5,6,7], other biomass [6,8,9,10] and waste [11,12,13,14], it can be seen that there are some differences with respect to the specific optimum process conditions found as well as large variations in the achievable TFN or NOx reduction degree. The latter is expected, as the fuel-N amount heavily influences the achievable reduction degree.

For demolition wood, the results are also quantitatively comparable, where TFN/Fuel-N below 10% and NOx reduction of typically 50-75% compared to non-staged operation were achieved experimentally. However, there is mostly a qualitative agreement regarding the influence of different operating parameters on the NOx reduction potential, but less so when it comes to the primary combustion zone temperature.

The reason for the differences can additionally be attributed to the actual fuel used and especially the fuel-N speciation and the choice of ideal plug flow reactors in this work, for the primary and secondary zone, while experimental conditions are not ideal. In practice a controlled and homogeneous addition of both primary and secondary air is challenging, as well as achieving a certain temperature level and a homogeneous temperature distribution. Mixing limitations will in practice result in a longer residence time needed compared to in an ideal flow reactor.

When comparing with earlier modelling results using an ideal plug flow reactor (Fig. 1, and [1,2], the main changes that can be seen are significant quantitative differences, which are directly attributed to chemical kinetics changes, while qualitatively similar results are found.

Additional parameters that are of importance are the choice of PFR or perfectly stirred reactor (PSR), the fuel-N content and speciation as mentioned, the relative fuel-C, fuel-H and fuel-O contents, the fuel moisture content, the main pyrolysis gas composition, the overall excess air ratio and the use of FGR (in the primary and/or secondary combustion zone).

The use of several air stages (primary and secondary) will not be significantly beneficial at ideal mixing conditions, but might be in a plant if improving the mixing conditions. From previous work [1] it can be expected that applying PSR will give quantitatively different but qualitatively comparable results.

The achievable TFN reduction will depend on the fuel-N content, giving increasing TFN reduction with increasing fuel-N content, due to higher concentrations of fuel-N intermediates, especially in TFN reducing reactions involving two N species.

Increasing NH_3/HCN ratio will increase the TFN reduction potential in the primary combustion zone. The relative fuel-C, fuel-H and fuel-O ratios influence the TFN reduction potential through changes in the competition for the radical pool as well as changes in the concentrations of fuel-N intermediates.

The fuel moisture content causes mainly a dilution effect at a constant temperature, giving lower TFN reduction. The main pyrolysis gas composition influences the TFN reduction through the radical pool, and elements and species enhancing the available radical pool for TFN reduction is beneficial.

The effect of an increasing overall excess air ratio, at a constant temperature, is that the O_2 concentration increases, speeding up the final burnout of CHO species, as well as reducing TFN species and N-intermediates concentrations, giving lower TFN reduction.

If applying FGR, to control/reduce temperatures, there is an additional effect influencing the N chemistry, through reduced O_2 concentrations for the same excess O_2 ratio, slowing down the CHO chemistry, which favors the fixed nitrogen to N_2 chemistry.

Further work will investigate in detail the extent of influence of these parameters on the achievable NOx reduction potential using the new mechanism and making effective reduced chemical kinetics mechanisms that could be applied in CFD simulations of real biomass and MSW combustion plants.

4. Conclusions

A large degree of TFN reduction, above 95% is possible by staged air combustion at optimum conditions. A number of factors influence the reduction degree, both fuel properties and process conditions.

From the ideal plug flow reactor simulations carried out in this work using a state-of-the-art detailed chemical kinetics mechanism, using demolition wood as fuel, the best primary combustion chamber temperature seems to be around 973 K and the best primary excess air ratio is in the range 0.8-0.9, from a practical point of view. Typically, 80% TFN reduction is then achievable.

However, the theoretical reduction potential is significantly higher, if having very good process control. Further work is needed to reduce the new detailed chemical kinetics mechanism, to be applied in CFD simulations.

Acknowledgements

References

[1] Skreiberg Ø, Becidan M, Hustad JE, Mitchell RE (2006). Detailed chemical kinetics modelling of NOx reduction by staged air combustion at moderate temperatures. Proceedings of the Science in Thermal and Chemical Biomass Conversion Conference, 30 August-2 September 2004, Victoria, BC, Canada, Vol. 1, pp. 40-54. Edited by A.V. Bridgwater and D.G.B. Boocock. CPL Press, UK.

[2] Houshfar E, Skreiberg Ø, Glarborg P, Løvås T. Reduced chemical kinetic mechanisms for NOx emission prediction in biomass combustion. International Journal of Chemical Kinetics 2012;44(4):219-231.

[3] Bugge M, Skreiberg Ø, Haugen NEL, Carlsson P, Houshfar E, Løvås T. Numerical simulations of staged biomass grate fired combustion with an emphasis on NOx emissions. Energy Procedia 2015;75:156-161.

[4] Bugge M, Skreiberg Ø, Haugen NEL, Carlsson P, Seljeskog M. Predicting NOx emissions from wood stoves using detailed chemistry and computational fluid dynamics. Energy Procedia 2015;75:1740-1745.

[5] Houshfar E, Skreiberg Ø, Løvås T, Todorović D, Sørum L. Effect of excess air ratio and temperature on NOx emission from grate combustion of biomass in the staged air combustion scenario. Energy & Fuels 2011;25(10):4643-4654.

[6] Houshfar E, Skreiberg Ø, Todorović D, Skreiberg A, Løvås T, Jovović A, Sørum L. NOx emission reduction by staged combustion in grate combustion of biomass fuels and fuel mixtures. Fuel 2012;98:29-40.

[7] Houshfar E, Khalil RA, Løvås T, Skreiberg Ø. Enhanced NOx reduction by combined staged air and flue gas recirculation in biomass grate combustion. Energy & Fuels 2012;26(5):3003-3011.

[8] Houshfar E, Løvås T, Skreiberg Ø. Experimental investigation on NOx reduction by primary measures in biomass combustion: Straw, peat, sewage sludge, forest residues and wood pellets. Energies 2012;5(2):270-290.

[9] Carroll JP, Finnan JM, Biedermann F, Brunner T, Obernberger I. Air staging to reduce emissions from energy crop combustion in small scale applications. Fuel 2015;155:37-43.

[10] Khodaei H, Guzzomi F, Patiño D, Rashidian B, Yeoh GH. Air staging strategies in biomass combustion-gaseous and particulate emission reduction potentials. Fuel Processing Technology 2017;157:29-41.

[11] Waldner MH, Halter R, Sigg A, Brosch B, Gehrmann HJ, Keunecke M. Energy from Waste – Clean, efficient, renewable: Transitions in combustion efficiency and NOx control. Waste Management 2013;33:317-326.

[12] Strobel R, Waldner MH, Gablinger H. Highly efficient combustion with low excess air in a modern energy-from-waste (EfW) plant. Waste Management 2018;73:301-306.

[13] Martin JJE, Koralewska R, Wohlleben A. Advanced solutions in combustion-based WtE technologies. Waste Management 2015;37:147-156.

[14] Speth K, Murer M, von Raven R, Spliethoff H. Influence of Stoichiometry and Mixing on NOx Reduction in Waste-to-Energy Plants. Energy Fuels 2016;30:10893-10899.

[15] http://logesoft.com/loge-software/

[16] Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. Modeling nitrogen chemistry in combustion. Progress in Energy and Combustion Science 2018;67:31-68.

[17] Løvås T, Houshfar E, Bugge M, Skreiberg Ø. Automatic generation of kinetic skeletal mechanisms for biomass combustion. Energy & Fuels 2013;27(11):6979-6991.