An Evaluation of Effects of Fuel Parameters and Flue Gas Recirculation on NOx Emissions through Detailed Chemical Kinetics Simulations

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In this work the effects of fuel parameters and under grate flue gas recirculation (FGR) are investigated when applying staged air combustion of solid fuel for the purpose of NOx reduction. In addition to temperatures, residence times and primary and overall excess air ratio, the fuel-N content and speciation, the relative fuel-C, fuel-H and fuel-O contents, the fuel moisture content, the fuel gas composition from the dry fuel and the use of FGR (in the primary and/or secondary combustion zone) influence the NOx reduction potential to a larger or smaller extent. To assess the influence of different parameters, a simulation matrix using one ideal plug flow reactor representing only the primary zone and a recent detailed chemical kinetics mechanism was carried out. The results show a large influence of the fuel-N content and speciation on the NOx reduction potential in the primary zone, and a significant influence of the fuel moisture content due to its fuel gas dilution effect. At the close to optimum NOx reduction conditions studied in this work (973 K, primary excess air ratio of 0.9), the influence of the fuel gas composition from the dry fuel on the achievable total fixed nitrogen reduction in the primary zone is relatively small, as well as its influence on the radical pool available for the fuel-N chemistry. The influence of the relative content of C, H and O in the fuel at a constant primary excess air ratio is also relatively small. From a kinetics point of view, there is a positive effect of applying under grate flue gas recirculation if the residence time is sufficiently long, however, the effect is relatively low compared to the other main influencing parameters. At higher temperatures the importance of the radical pool availability as well as its speciation increases, and a more significant part of the NH_3 and especially HCN reduction in the primary zone results in increasing NO formation with increasing temperature.

1. Introduction

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 a previous work (Skreiberg et al., 2019) a recent detailed chemical kinetics mechanism (Glarborg et al., 2018) was used to investigate the NOx reduction potential by staged air combustion at different operational conditions (primary excess air ratio, overall excess air ratio, temperature in the primary and secondary zone/reactor, residence time), using two ideal plug flow reactors connected in series. This enabled 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 showed, for demolition wood as fuel, a large NOx reduction potential, as high as above 95% Total Fixed Nitrogen (TFN = total mass of N in NH_3, HCN, NO, NO_2, N_2O) reduction at theoretically optimum conditions. Through reaction path analyses the main reaction pathways and reactions could be identified. A similarly high TFN reduction potential for

demolition wood has also been shown experimentally by Houshfar et al. (2011), at similar staged air conditions.

Based on previous work: 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 is expected to increase the TFN reduction potential in the primary combustion zone. The relative fuel-C, fuel-H and fuel-O contents influence the TFN reduction potential through changes in the competition for the radical pool (OH, O, H) 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 fuel gas composition influences the TFN reduction through the radical pool, and elements and species enhancing the available radical pool for TFN reduction is expected to be 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 favours the fixed nitrogen to N_2 chemistry. In this work the extent of influence of these parameters on the achievable NOx reduction potential is investigated at earlier identified close to optimum TFN reduction conditions (Skreiberg et al., 2019) in the primary zone using the recent mechanism by Glarborg et al. (2018), which was also used by Skreiberg et al. (2019), to reveal their importance and understand their influence.

The final goal would be to arrive at computationally effective but accurate enough 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. Then knowledge of the main parameters influencing the kinetics and the main reaction pathways are important.

2. Methods

The software LOGEresearch (LOGEresearch, 2019) 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. (2018). 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 is a comprehensive (148 species and 2764 reactions) and up-to-date mechanism including CHO chemistry (based on CH_4 and hydrocarbons up to C_2H_6) and N chemistry, updated to the current level of knowledge regarding species, reactions, rate constants and thermochemistry.

A fuel gas composition representing demolition wood (with a fuel-N content of 1.06 wt% on dry ash free basis and a moisture content of 12.33 wt% and an ash content of 2.18 wt% on wet basis) was used in previous works (Løvås et al., 2013; Skreiberg et al., 2019), and this was adopted also in the current work. The fuel-C, fuel-H and fuel-O contents were respectively 48.43, 6.36 and 44.15 wt% on dry ash free basis. The fuel-N level in the fuel gas was set according to the fuel-N content, distributed in the base case on NH_3, HCN (HCN/NH_3 ratio of 0.65) and a small amount of NO (5 % of the fuel-N content). The base case residence time was set to 1 s, and the pressure was set to atmospheric.

To investigate the effect of the different influencing parameters mentioned, a simulation matrix was set up. A primary excess air ratio of 0.9 and a primary zone temperature of 973 K were maintained in all simulations except when investigating the influence of temperature, as this was found to be a good choice for achieving a high NOx reduction degree in the primary zone in the earlier work (Skreiberg et al., 2019). The fuel-N content, except when investigating the influence of this, was set constant. However, depending on variations in other parameters, the concentration of fuel-N species in the primary zone mixture vary to some degree. This is unavoidable, and therefore TFN/Fuel-N was evaluated also with respect to the resulting change in the concentration of fuel-N species in the primary zone mixture.

3. Results and discussions

First the primary zone TFN/Fuel-N for different fuel-N content and speciation was investigated. The influence of the fuel-N content was investigated by reducing the fuel-N content to 10% (lowN) and 50% (halfN) of the base case fuel-N content (1.06 wt% N). The influence of the N speciation was investigated by increasing the HCN/NH_3 ratio to 1/0.65 (moreHCN) compared to 0.65 in the base case, and by only including NH_3 (noHCN) or only HCN (noNH3) as fuel-N species in addition to the small amount of NO which was always set to 5% of the fuel-N content. Figure 1 (left) shows the resulting TFN/Fuel-N for the primary zone and the final TFN distribution at 1 s residence time (right), also comparing with the base case. As expected, the TFN reduction degree in the primary zone heavily depends on the fuel-N content, giving an exponentially increasing

TFN/Fuel-N with decreasing fuel-N contents. Regarding fuel-N speciation, increasing HCN content relative to the NH_3 content increases TFN/Fuel-N, which can be explained by the higher potential for final N_2 formation from NH_3 compared to HCN, based on the available chemical kinetics pathways (Skreiberg et al., 2019).
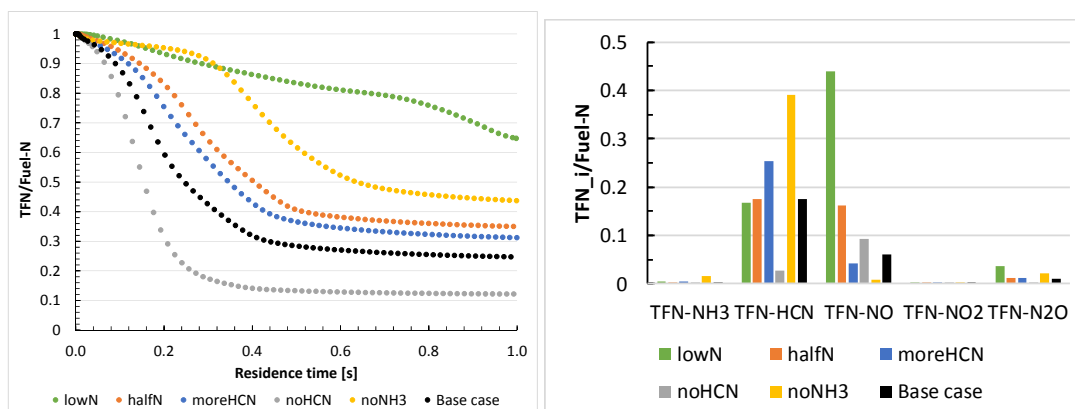

Figure 1: Left: Primary zone TFN/Fuel-N for different fuel-N content and speciation. Right: The final TFN distribution at 1 s residence time.

The influence of different fuel gas speciation was investigated by increasing or decreasing with 10% the levels of H_2 (moreH2, lessH2), CxHy (moreCxHy, lessCxHy) and CO (moreCO, lessCO) compared to the base case. The fuel elemental composition was always preserved in these cases, meaning that more or less of one species resulted in a corresponding decrease in other species to preserve elemental balances and a primary excess air ratio of 0.9. Figure 2 shows the resulting TFN/Fuel-N for the primary zone, also comparing with the base case. The effect of these variations on TFN/Fuel-N is relatively small. Increasing the amount of H_2 slightly reduce TFN/Fuel-N, while increasing the amount of CO is more effective, reducing TFN/Fuel-N more. On the other hand, increasing the amount of CxHy increases TFN/Fuel-N. This indicates that hydrocarbons consume more radicals towards their final products CO_2 and H_2O and hence limits the NOx reduction potential more than H_2 and especially CO which is mainly reacting with OH to directly form CO_2 and H. However, the normalised time-integrated radical levels shown in Figure 2 (right) indicates that the picture is more complex, and that more detailed reaction paths analyses are needed to assess the role and importance of radical availability as a function of residence time at the different conditions.
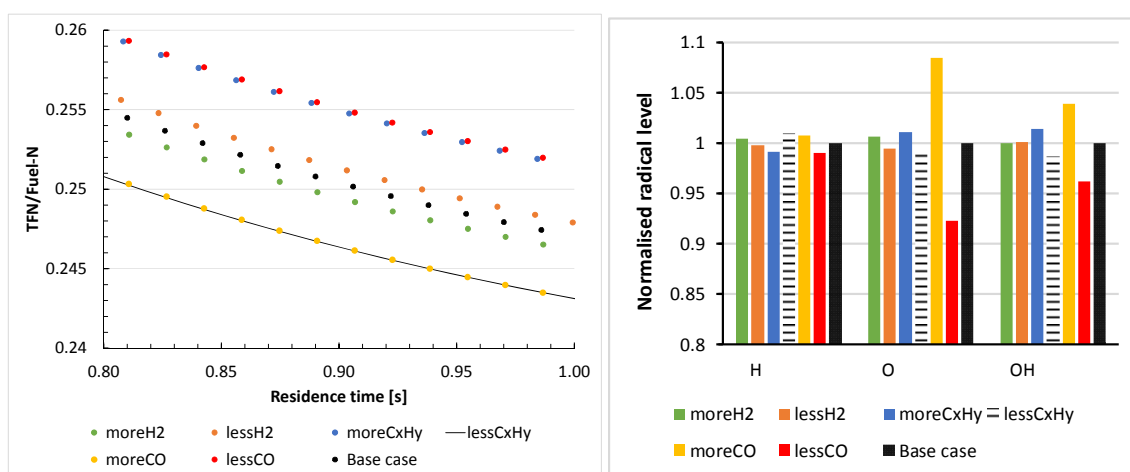

Figure 2: Left: Primary zone TFN/Fuel-N for different fuel gas speciation. Right: Normalised time-integrated radical levels over the 1 s residence time period.

The influence on primary zone TFN/Fuel-N of different moisture contents and when applying under grate FGR was investigated by doubling (moreMoist) or removing (noMoist) the moisture, and by using 20% recirculated flue gas and 80% air in the FGR case, giving 18.16 vol% O_2 in the recirculated flue gas and air mixture for an overall excess air ratio of 1.6. Figure 3 shows the resulting TFN/Fuel-N for the primary zone, also comparing

with the base case. As can be seen, doubling the moisture content significantly increases TFN/Fuel-N, while the opposite effect can be seen when removing the moisture content. The reason for this is the dilution effect that the moisture content represents. The effect of this is similar to the effect of fuel-N concentrations, i.e. the moisture content directly influences the concentration of fuel-N species in the fuel gas. Decreased fuel-N concentrations, due to moisture dilution, means that the typical reactions involving two fuel-N species leading to N_2 formation are penalised more than the typical reactions involving one fuel-N species leading to NO formation. Compared to the base case, under grate FGR slightly reduces TFN/Fuel-N if the residence time is sufficiently long. The recirculated flue gas reduces the oxygen concentration, thereby retarding the CHO chemistry. This results in a delayed TFN reduction until the CHO chemistry has been halted, where after a small positive effect can be seen, due to the positive influence of FGR on the radical pool with increasing residence time (Figure 3, right). Typically, the radical formation starts with OH followed by O and H, while the O level drops first, followed by OH and H.
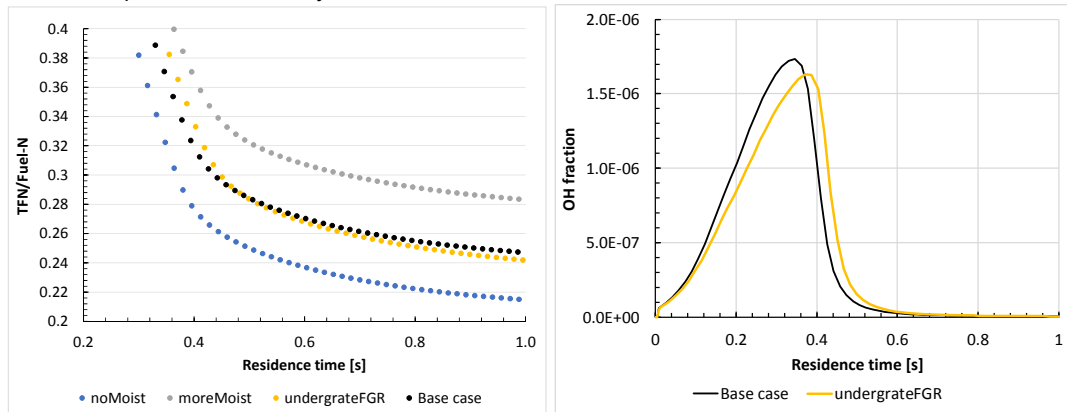

Figure 3: Left: Primary zone TFN/Fuel-N for different moisture contents, and also comparison with under grate FGR. Right: OH radical fraction for under grate FGR and the base case.

Regarding FGR in the secondary zone, the effect of this at otherwise unchanged temperature and overall excess air ratio conditions, is a reduction in the oxygen concentration, giving lower TFN/Fuel-N. At the same time, the FGR dilutes the remaining TFN content, giving higher TFN/Fuel-N. Hence, the chemical effects of the FGR can be rather minor and go in both directions. The main benefit of FGR in the secondary zone in practical applications is connected to temperature control, i.e. preventing high temperatures and temperature peaks that otherwise will result in increased NOx formation through potentially also other NOx formation pathways. Finally, the influence of the fuel element contents was investigated increasing (moreC, moreH) or reducing (lessC, lessH) the contents of C and H with 10%. Figure 4 shows the resulting TFN/Fuel-N for the primary zone, also comparing with the base case.
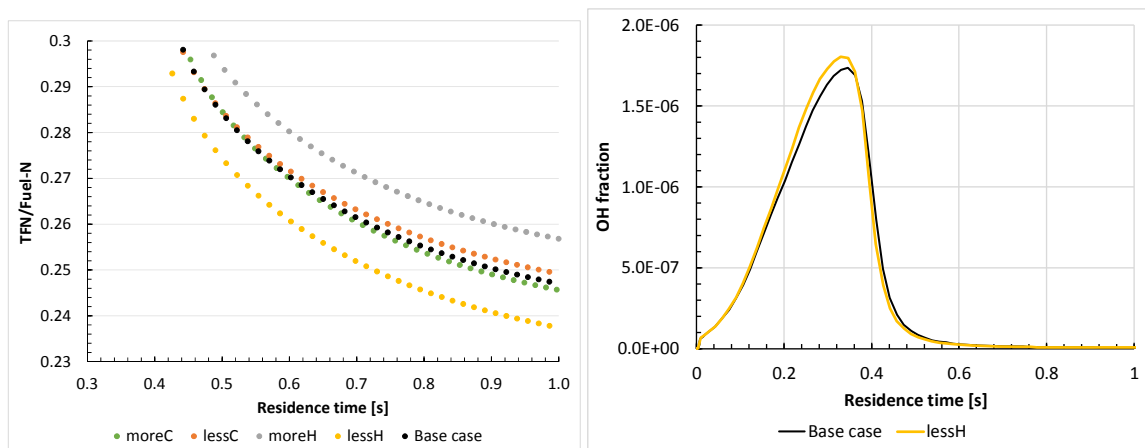

Figure 4: Primary zone TFN/Fuel-N for different fuel element contents. Right: OH radical fraction for the lessH case and the base case.

As can be seen, more or less C hardly affects TFN-Fuel-N, but as it at the same time significantly influences the fuel-N concentration, more C leads to a lower TFN/Fuel-N at lower fuel-N concentration, i.e. improving the NOx reduction. More H increases TFN/Fuel-N somewhat and less H similarly reduces it. Less H also increase the OH level (Figure 4, right). However, more H also leads to lower fuel-N concentration, partly explaining the increased TFN/Fuel-N. To achieve a reduction or increase in the C and H contents, the O level in the fuel was changed accordingly. A primary excess air ratio of 0.9 was always preserved.

As the temperature and primary excess air ratio always were kept constant, the resulting TFN/Fuel-N for a given fuel-N speciation mainly depends on the resulting fuel-N concentration in the mixture with primary air, and in addition the influence of this mixture on the radical pool available for the fuel-N chemistry as a function of residence time. Hence, plotting TFN/Fuel-N as a function of the fuel-N concentration in the mixture should reveal a clear trend, with deviations along this trend line influenced by radical pool availability. As shown in Figure 5, the trend as a function of the fuel-N concentration in the mixture is clear. However, significant deviations can be seen, which can be explained by radical pool availability. Figure 6 zooms in on the influence of the fuel gas composition from the dry fuel. In the case of improved TFN reduction more radicals are available for the fuel-N chemistry. Hence, a higher degree of reduction of fuel-N species to N_2 results. However, as can be seen, the picture is complex, as the trends are not constant with respect to the influence of the individual gas species.
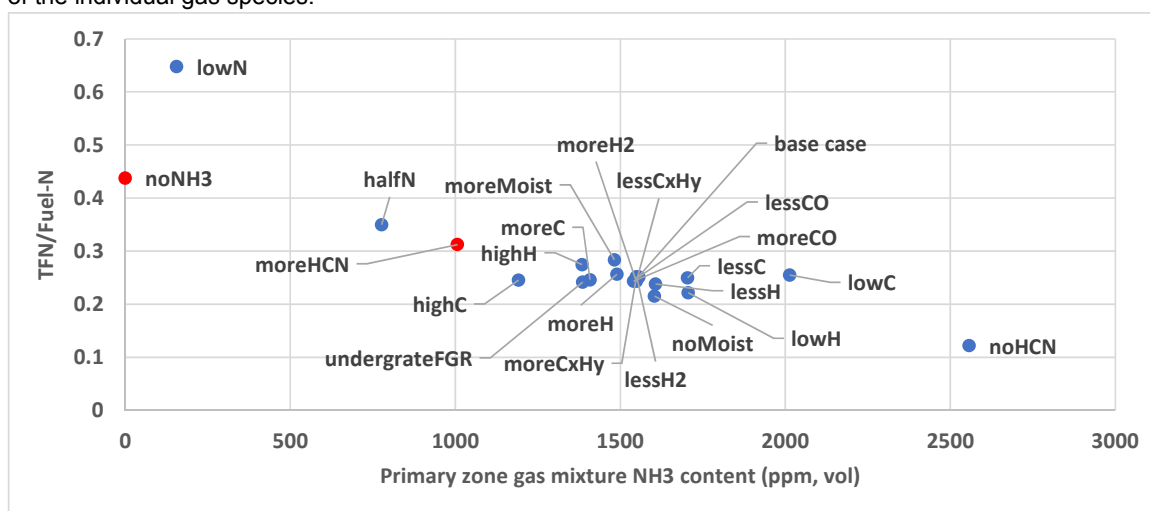

Figure 5: TFN/Fuel-N as a function of resulting NH_3 concentration in the different cases. Additional "high" (30% more) and "low" (30% less) cases were included for the influence of the relative fuel elemental composition.
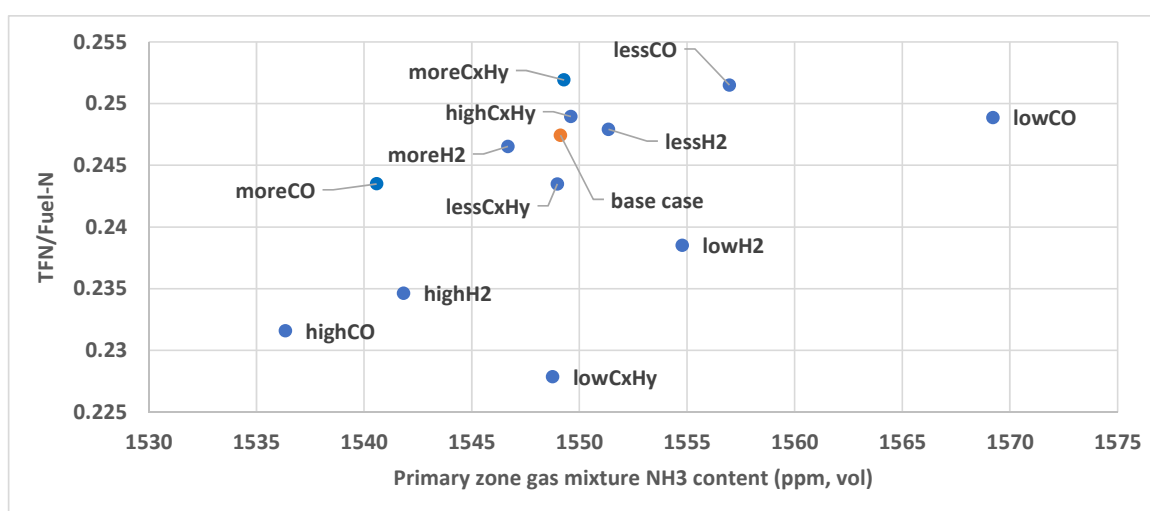

Figure 6: Zoom in on TFN/Fuel-N as a function of resulting NH_3 concentration for the fuel gas speciation cases. Additional "high" (30% more, except for CO with 15% more) and "low" (30% less) cases were included for the influence of the fuel gas composition.

Figure 7 (left) shows the influence of temperature at the base case conditions and the final TFN distribution at 1 s residence time (right), where the TFN reduction degree is reduced with increasing temperature above the base case temperature, which is the optimum temperature, while at the lower temperature of 873 K the TFN reduction degree drops again and longer residence time is needed. This can be explained by the temperature influence of the CHO chemistry as well as of the N chemistry and the resulting radical pool availability for the TFN reduction, resulting in increasing NO formation in the primary zone with increasing temperature.
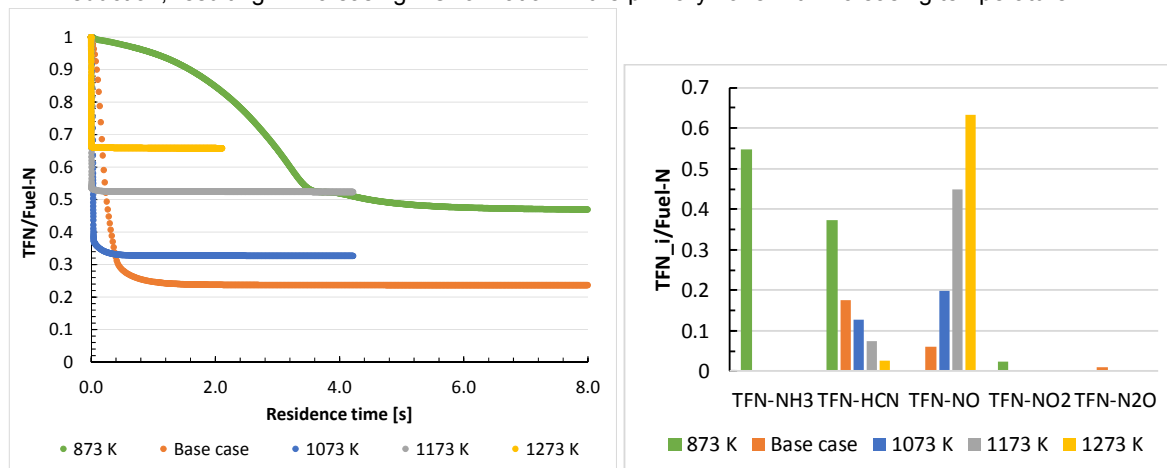

Figure 7: Left: TFN/Fuel-N as a function temperature at the base case conditions. Right: The final TFN distribution at 1 s residence time.

4. Conclusions

A large degree of TFN reduction 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, at a primary combustion chamber temperature of 973 K and a primary excess air ratio of 0.9, 75.26% TFN reduction was achieved in the primary zone in the base case. An additional TFN reduction of 3.23% can be achieved for a dry fuel giving less H_2O that otherwise dilutes the fuel gas. When adding secondary air, an additional reduction of the remaining TFN will occur. If applying under grate flue gas recirculation this has a small positive effect. The practical influence of other parameters as the fuel gas speciation and the relative C, H and O content in the fuel is relatively small at the selected base case temperature and primary excess air ratio, indicating a relatively low influence of competition for the radical pool. However, this influence increases at higher temperatures. Further work is needed to reduce, while preserving the important chemical kinetic pathways, the new detailed chemical kinetics mechanism, to be applied in CFD simulations.

Acknowledgments

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