Assessment of Transient NOx Reduction Potential in Wood Stoves

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NOx emissions from wood stoves remain a significant concern, even though modern wood stoves are continuously improved regarding emissions due to incomplete combustion, e.g. particulates of organic origin. Today, state of the art wood stoves applies staged air combustion. This air staging is the main reason that new wood stoves have much lower levels of particulate emissions than older ones. An optimized two-stage combustion should also be able to significantly reduce the NOx emission level. So far, however, this has not been emphasized sufficiently well when it comes to wood stoves.

In this work, a recent comprehensive detailed chemical kinetics mechanism is used, together with zero-dimensional homogeneous reactors (plug flow and perfectly stirred reactors) and a transient fuel conversion model including NOx precursors release. This enables calculating the transient NOx emissions and the fuel-N to N_2 reduction degree as the batch combustion process progresses for different mixing configurations. Key parameters are varied to assess the NOx reduction potential. Based on this, guidelines can be proposed on how to achieve an optimum NOx reduction. The knowledge derived will be useful for further computational fluid dynamics (CFD) work, in combination with experimental validation.

In wood stove experiments, typically two-thirds of the fuel-N is not emitted as NOx ($NO+NO_2$), even for a low nitrogen containing wood specie as spruce. This is true also for old wood stoves without staged air combustion. Hence, the majority of the fuel-N is converted to N_2, or partly also released as NOx precursors (mainly NH_3 and HCN). Emission of N_2O from wood stoves has been shown experimentally to be of little significance.

The detailed chemical kinetics simulations carried out in this work using ideal reactors show that a very significant reduction of fuel-N to N_2 can take place for fuel and operating conditions relevant for wood stoves, especially if applying a perfectly stirred reactor. The best case, for a perfectly stirred reactor, gives a total fixed nitrogen to fuel-N ratio of 0.55 in the gas phase. This reduces to 0.45 when accounting for char-N directly forming N_2.

However, this is still too little to reach the experimentally measured values in non-staged and non-optimised staged air wood stove experiments. This indicates that more work is needed on 1) assessing the total amount of nitrogen containing emissions from wood stoves, 2) the importance of heterogeneous reactions (direct formation of fixed nitrogen species from the char oxidation and reduction of fixed nitrogen species on char surfaces), and 3) using CFD to resolve the detailed mixing conditions in combination with accounting for the detailed gas phase and heterogeneous reaction kinetics. For this also a detailed enough model of the integration and conversion of the solid fuel throughout the batch combustion cycle is needed.

1. Introduction

Improved models and modelling approaches, in combination with targeted experiments, are keys in the development of future's downscaled clean burning and energy efficient wood stoves. These downscaled wood stoves may potentially also have significantly reduced NOx emissions.

As a step towards achieving a significant NOx reduction by optimized staged air combustion, it would be interesting to assess the reduction potential by modelling based tools. This should be done by using detailed chemical kinetics in ideal or stochastic reactors, and ultimately also in computational fluid dynamics (CFD) simulations. Based on the derived knowledge, changes in design and operational procedures can then be proposed to reduce NOx emissions, while not increasing other emissions.

The transient nature of combustion of wood logs in wood stoves is a result of the batch loading principle of these units, i.e. the fuel is loaded as a batch, and then the batch is combusted during a relatively long time period (up to several hours) without additional fuel loading. This influence both efficiencies (combustion, thermal) and emissions throughout the transient combustion cycle. The consequence of the batch loading is that the moisture content is evaporated at its maximum rate in the initial phase of the batch cycle, followed by devolatilization of the volatile content of the fuel, and finally the char burnout. Hence, the stove power in the beginning of the batch cycle will be low due to moisture evaporation, thereafter increasing rapidly towards a maximum due to an accelerating devolatilization rate of the whole batch and decreasing again as the char is combusted at a much lower rate. The high heating value of the char compensates somewhat for the latter effect. If loading a new batch before the current one has been completely combusted this new batch will go through the same transient process.

The emission levels during the transient combustion cycle can vary significantly, especially regarding emissions of unburnt (CO, hydrocarbons, particles), and also depend on the thermal state of the stove when a batch is loaded. However, when it comes to NOx, the emission levels are less fluctuating. The NOx is formed from the fuel nitrogen, and even for a low nitrogen wood species such as spruce, typically two-thirds of the fuel nitrogen is not converted to NOx but is ideally converted to molecular nitrogen. However, at low temperatures some of the intermediate nitrogen species released with the volatiles, typically NH_3 and HCN, might survive the combustion chamber and will be emitted to the atmosphere. There is evidence that this might happen, and e.g. in the Norwegian national emission inventory, there is an emission factor for NH_3 for wood stoves, of 0.066 g/kg dry wood (Seljeskog et al., 2017). Hence, the somewhat lower NOx emission levels observed at part load operation and lower average temperatures might not mean lower fixed nitrogen emissions. I.e. the temperature influence on the total fixed nitrogen (TFN) emissions might be limited. If carrying out detailed chemical kinetics simulations using ideal reactors for the conversion of NH_3 or HCN as fuel-N intermediates in the volatiles released, the temperature needed for their complete conversion at over-stoichiometric conditions is relatively high, about 700°C for NH_3 and higher for HCN, for a realistic residence time.

The scientific literature concerning NOx emission from wood stoves is scarce, even though a number of other works reports on measured NOx emissions, but rarely emissions of other fixed nitrogen species.

Skreiberg (1997) reported on NOx emission from wood stoves, from spruce, pine and birch, and for an old wood stove, a staged air emission wood stove equipped with a catalytic converter and a downdraft staged air wood stove. The conversion of fuel-N to NOx was found to be lowest in the downdraft staged air stove and highest in the stove equipped with a catalytic converter. The average conversion of fuel-N to NOx was below 0.4 for all stoves when using spruce. Overall, the values could be found within a relatively modest range considering the three different wood stove technologies tested, the range of operating conditions tested and the use of both softwood and hardwood. N_2O emission was measured for selected experiments and was found not to contribute significantly. NOx emissions both before and after the catalytic converter were measured in selected experiments, showing significantly higher emission levels after the catalytic converter.

Other works not involving wood stoves do show a clear influence of the fuel-N content and operating conditions on the degree of conversion of fuel-N to NOx, in experiments (Houshfar et al., 2011) and in simulations (Skreiberg et al., 2019a,b). It might be that the operating conditions and the air flow patterns in a wood stove already introduces considerable reduction potential and that little further reduction can be achieved in non-optimised staged air combustion units. It might also be that heterogeneous reduction reactions are more important than anticipated. In addition, other nitrogen emissions than NOx may play a significant role during parts of the combustion cycle, as well as nitrogen contained in tars. In general, there is a need for more experimental, modelling and simulation work to understand, model and simulate what is really going on. When it comes to NOx emission limits for wood stoves, they mostly do not exist, only a few countries have introduced emission limits, however, the focus on NOx emissions is expected to increase. Current emission limits are set so high, since reducing the NOx emissions is challenging, that no one in practise have problems with getting below these limits, without introducing measures to reduce the NOx emissions. Hence, there are no real incentives for improving wood stoves with respect to NOx emissions. In the end this might also be very challenging, due to the large reduction of fuel-N to molecular nitrogen that naturally already takes place. Anyway, the potential for further NOx reduction should be carefully assessed, and if an optimised staged air combustion could significantly further lower the NOx emissions from wood stoves. This work is a contribution to that aim.

2. Methods

In this work, a recent comprehensive detailed chemical kinetics mechanism is used, together with both two ideal plug flow reactors (PFR) and two ideal perfectly stirred reactors (PSR) in series, and combined with a transient fuel conversion model including NOx precursors release. This enables calculating the transient fuel-N to N_2 reduction degree as a wood log batch combustion process progresses.

The software LOGEresearch (LOGEresearch, 2019) has been used for the simulations and kinetics analysis, using the plug flow and perfectly stirred reactor modules in combination with the detailed chemical kinetics mechanism of Glarborg et al. (2018), which 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 transient fuel gas composition representing spruce wood, with a low fuel-N content of 0.07 wt% on dry ash free basis and a moisture content of 18 wt%, was used. The fuel-C, fuel-H and fuel-O contents were respectively 47.25, 6.30 and 46.38 wt% on dry ash free basis. The fuel-N level in the fuel gas was set according to the fuel-N content, assumed as NH_3 in the base case. NO and N_2 was included as the products of heterogeneous char reactions. The effect of replacing NH_3 with HCN was also investigated. The reactor pressure was set to atmospheric and primary zone (where primary air is added) residence time to 2 s in the base case and secondary zone residence time to 1 s. The effect of reducing the primary zone residence time was also investigated. Primary excess air ratio and primary zone temperature were varied, and secondary zone temperature was kept the same as in the primary zone while total excess air ratio was set to 1.5 in the volatiles combustion period and increasing to 2.2 in the char combustion period. The TFN to fuel-N ratio (TFN/Fuel-N) was calculated to assess the NOx reduction degree. TFN in this work includes all N-species except N_2. NH_3, HCN, NO, NO_2 and N_2O are the main TFN species. However, at low temperature and low primary excess air ratio, also other intermediate N-species may exist in significant amounts.

A transient gas release model was developed, releasing all the volatile fuel-N as N-intermediates, while the char-N was released as NO and N_2, as these are the main N-species resulting from the char combustion. In this work the transient distribution between NO and N_2 from char-N was set fixed to 50/50, which is a simplification. A typical transient mass loss behaviour of a wood stove was applied, using Fuelsim-Transient (Skreiberg, 2002). This software enables distributing the release of C, H, O and N in the wood over the duration of the combustion cycle and accounts as well for the transient drying process. The developed transient gas release model provided the transient release of the pyrolysis gas, fulfilling the overall elemental balances as well as an energy balance. Figure 1a shows fuel-N species concentrations and primary excess air ratio as a function of time for a case with primary excess air ratio of 0.8 in the volatiles combustion period and a primary zone temperature of 1073 K, as well as the transient primary excess air ratio. The model assumes that no char is consumed in about the first 30% of the combustion cycle, and hence no char-NO is formed, whereafter char is oxidised in increasing amounts.
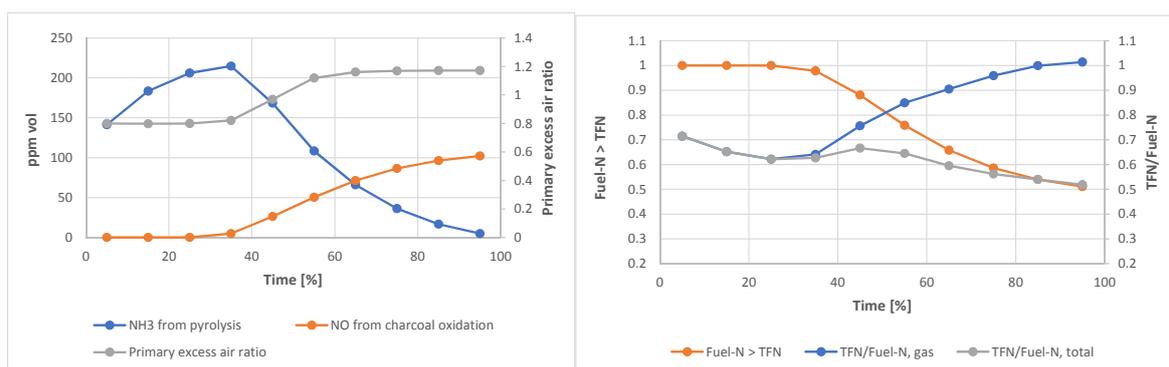
Figure 1: Left(a): Fuel-N species concentrations and primary excess air ratio as a function of time for a case with primary excess air ratio of 0.8 in the volatiles combustion period and a primary zone temperature of 1073 K. Right(b): Amount of fuel-N released to the primary zone as TFN (Fuel-N > TFN) and TFN remaining after the primary combustion stage for a primary excess air ratio of 0.8 and a temperature of 1073 K.

When assessing the TFN reduction potential in the primary zone, TFN/Fuel-N was calculated for the primary zone reactor and in addition, the direct formation of N_2 from the char was accounted for. Figure 1b shows the amount of fuel-N released to the primary zone as TFN and the TFN remaining after the primary combustion

stage for a primary excess air ratio of 0.8 and a temperature of 1073 K, showing a certain influence of the transient fuel gas composition.

3. Results

A simulation matrix was set up to investigate the influence of various parameters on the transient NOx reduction potential given by TFN/Fuel-N, in both the primary and secondary zone as well as the total. A base case was selected, with a temperature of 1073 K and primary excess air ratio of 0.8. TFN/Fuel-N (for fuel gas TFN) for the base case is shown in Figure 2 for both a PFR and a PSR. As can be seen, the TFN reduction degree varies throughout the transient combustion cycle and with the largest reduction degree where the NH_3 level in the fuel gas is the highest, since the speed and the extent of the reducing reactions depend on the N-species' concentrations. Comparing the PFR and the PSR, it becomes clear that these two ideal reactors, representing extremes of mixing conditions relevant for wood stoves depending on the physical location in the combustion chamber, yields quite different TFN reduction degree. Compared to the PFR, the PSR yields a rather distinct optimum in the primary zone at a primary excess air ratio close to unity, and a significant further TFN reduction occurs in the secondary zone for sub-stoichiometric conditions in the primary zone, in contrast to the PFR.
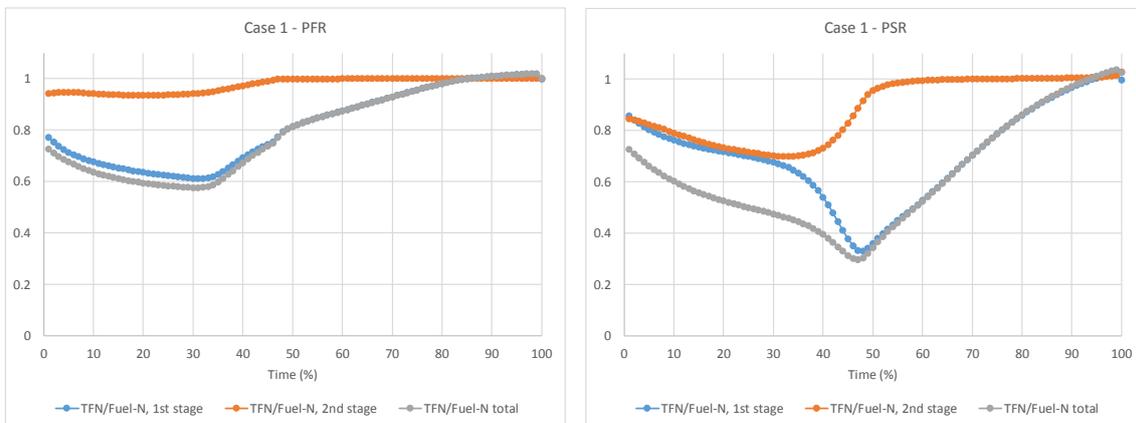
Figure 2: Base case with 1073 K and λ_P=0.8.

If increasing the temperature from 1073 to 1173 K and the primary excess air ratio from 0.8 to 0.9, the PFR yields a lower TFN reduction degree, as shown in Figure 3. For the PSR, however, the TFN reduction degree increases, in both the primary and the secondary zone.
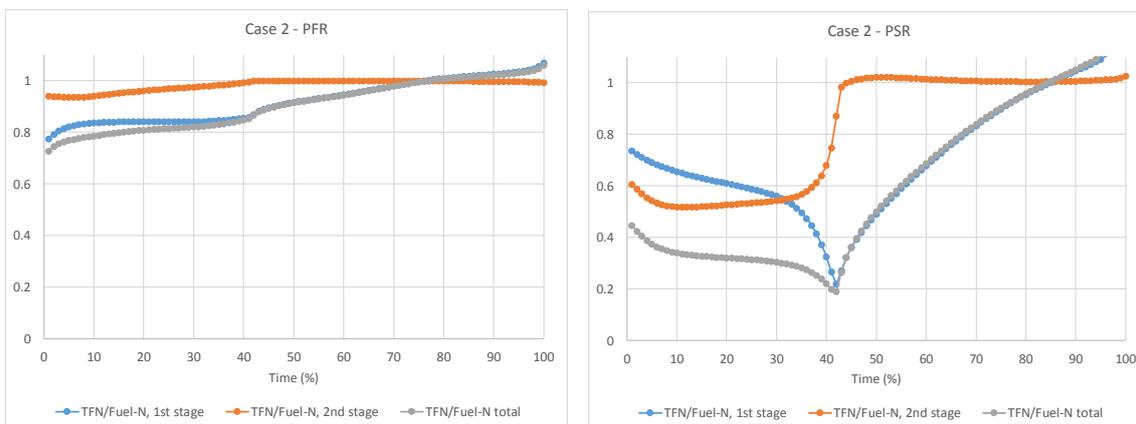
Figure 3: Case with 1173 K and λ_P=0.9.

The maximum reduction of gas phase TFN occurs when the TFN concentration is the highest, which is between 30 and 40% of the total time period. Figure 4 shows TFN/Fuel-N in the primary zone for different

combinations of primary excess air ratio and temperature in this time period. A significantly higher reduction is achieved in the PSR reactor, with an optimum primary excess air ratio around stoichiometric and at a temperature of 1073-1173 K. For the PFR, the optimum is for a primary excess air ratio of 0.7-0.8 and a temperature of 1073-1173 K. Hence, the mixing conditions clearly influence the optimum primary excess air ratio, while the optimum temperature is similar. For the lowest temperature of 973 K, also significant amounts of other N intermediates than NO, NO_2, N_2O, NH_3 and HCN exist, due to an overall slower chemistry at this relatively low temperature. When adding the secondary air, a further TFN reduction will occur, and the reduction degree depends on the remaining TFN level and speciation in addition to the process conditions; temperature, residence time and overall excess air ratio.
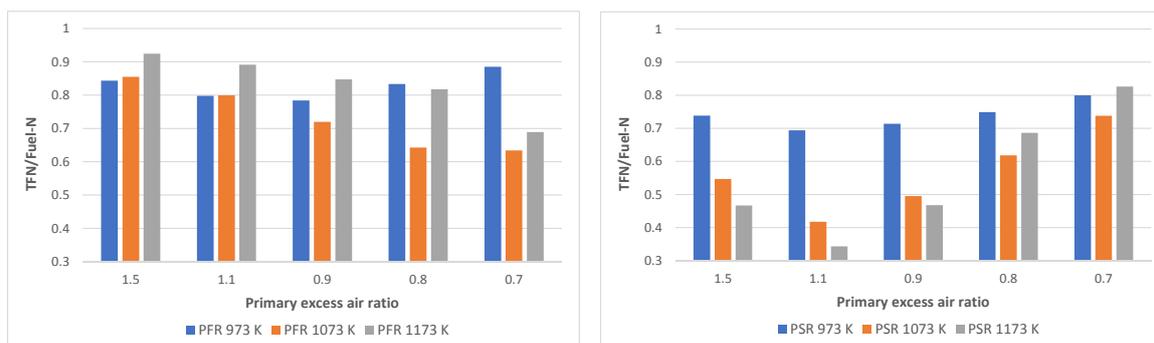
Figure 4: TFN/Fuel-N for different combinations of primary excess air ratio and temperature between 30 and 40% of the total time period.

Figure 5 shows, for selected combinations of primary excess air ratio and temperature, primary, secondary and total TFN/Fuel-N and in addition includes the direct reduction of char-N to N_2, for the complete transient combustion cycle. The results are sorted according to the total TFN/Fuel-N. The achievable reduction degree in the secondary zone is limited, especially in the PFR, as the remaining TFN after the primary zone contains more TFN in the form of NO and less in the form of NH_3. For the PFR the best case gives a total TFN/Fuel-N of 0.77, reducing to 0.63 when accounting for char-N to N_2. The best case for the PSR gives respectively 0.55 and 0.45.
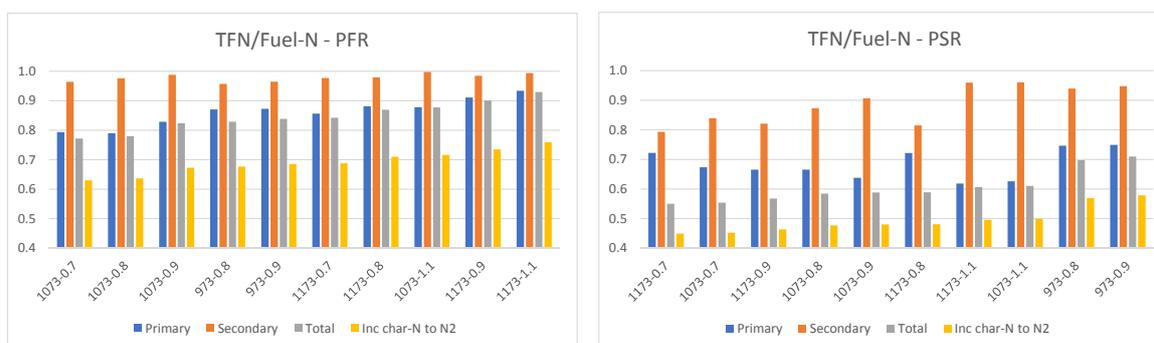
Figure 5: TFN/Fuel-N for different combinations of primary excess air ratio and temperature.

The residence time influences the TFN reduction degree, with an increased TFN/Fuel-N reduction with increased residence time. However, the effect of an increasing residence time decreases rapidly as the temperature increases, and also with increasing primary excess air ratio. For e.g. a residence time of 0.25, 0.5, 1 and 2 s, the TFN/Fuel-N becomes 0.99, 0.77, 0.644, 0.642 for a primary excess air ratio of 0.8 and a temperature of 1073 K in the PFR. In the PSR the corresponding values are 0.90, 0.77, 0.68, 0.62. If replacing NH_3 with HCN as fuel-N species, the TFN reduction potential decreases with increasing HCN replacement (Skreiberg et al., 2019b).

The reason for the PSR giving a higher TFN reduction degree than the PFR is the influence of mixing conditions on the radical pool available for the nitrogen chemistry, due to competition with the main chemistry. In the PSR the concentrations inside the reactor are the same as at the reactor outlet, which slows down the

main chemistry and which is beneficial for the radical pool available for the nitrogen chemistry. In the PFR, the concentrations of reactants are high at the reactor inlet, giving initially fast conversion of the main reactants and overall faster conversion, limiting the overall amount of radicals available for the nitrogen chemistry.

4. Conclusions

In this work, it has been demonstrated through detailed chemical kinetics simulations using ideal reactors that a substantial reduction of TFN can be achieved throughout a wood log combustion cycle in wood stoves when applying staged air combustion. Optimum conditions exist, where the TFN reduction is maximised. Depending of the choice of ideal reactor, the achievable TFN reduction varies, with in general a higher TFN reduction for a PSR compared to a PFR. These two ideal reactors represent extremes of mixing conditions relevant for wood stoves depending on the physical location in the combustion chamber. Wood log combustion in wood stoves is a highly transient combustion process, and the highest TFN reduction potential coincides with the highest levels of fuel-N release from the wood logs. If comparing our current numerical results with measured NOx emission levels from wood stoves, and the resulting TFN/Fuel-N degree, there is a gap, meaning that more of the fuel-N is seemingly converted to N_2 in wood stove experiments. This indicates that there are emissions of N-intermediates, e.g. NH_3 and HCN, that are not accounted for when carrying out such wood stove experiments. This is acknowledged in the Norwegian national emission inventory, where there is an emission factor for NH_3 for wood stoves. Typically, the temperature needed for the complete conversion of HCN is higher than for NH_3. Clearly, there is a potential for enhancing the TFN reduction in wood stoves, at optimum conditions. However, this requires adequate control of the transient combustion process. Further work should aim at maximum TFN reduction including eliminating emissions of nitrogen intermediates such as NH_3 and HCN. This requires sufficient temperatures and optimisation of the primary air addition. For a PFR and a PSR, a TFN/Fuel-N of 0.63 and 0.45 was achieved, which even for the PSR is poorer than experimentally measured TFN/Fuel-N levels, in experiments where no optimisation of the air distribution to reduce NOx emissions has been carried out. One can therefore postulate that a significant amount of fuel-N intermediates might be released directly during poor (low temperature) wood stove combustion experiments. Therefore, it is considered very important to be able to model and account for this correctly, such that the TFN released into the atmosphere from wood log combustion in wood stoves can be reduced.

Acknowledgments

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