Homogeneous Oxidation of Volatile Nitrogen (NH_3, HCN) to Nitrogen Oxides: A Modeling Study of the Effect of Alkali Vapors

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Abstract

The effect of alkali vapors in the combustion of different types of Scandinavian fuels, i.e. Finnish black liquor, Swedish wood and Danish straw, was studied based on detailed chemical kinetic modeling. Two H/C/O/N/Na/K mechanisms consisting of about 350 reactions between 60 chemical species were utilized and validated with available experimental data from the literature. The agreement with the experimental results was satisfactory. The results demonstrated that the alkali species studied, i.e. Na and K, promote the NO_x reduction in the air staged or non-staged combustion systems. The presence of alkali metals increased the optimum temperature from ca. 1073-1173 K (no alkali cases) to ca. 1273-1373 K (alkali cases) due to the removal of the radicals via the following sequence:

$$NaOH + H \rightarrow Na + H_2O \qquad \text{\{R254\} (1)}$$

$$Na + O_2 + M \rightarrow NaO_2 + M \qquad \text{\{R242\} (2)}$$

$$NaO_2 + OH \rightarrow NaOH + O_2 \qquad \text{\{R260\} (3)}$$

$$\overline{}$$

$$H + OH \rightarrow H_2O \qquad (4)$$

which leads to a net formation of water (H_2O) from H and OH. The same trend was observed for K chemistry. Sensitivity and reaction path analysis was applied to investigate the most crucial reactions on the predictions.

Key words: Alkali, NO_x reduction, Chemkin, Kinetic modeling.

Introduction

Global climate warming has become an issue of tremendous importance. Carbon dioxide (CO_2) is the main component that produces the greenhouse effect, leading to an increase in the temperature of our planet. Biomasses are an alternative to fossil fuels and they lead to no net-CO_2 emission. The use of these "green fuels" is expected to grow steadily in the future. Nitrogen oxides (NO_x, N_2O) are also considered pollutants of the environment. Nitrous oxide (N_2O) is an important component of the greenhouse gas emissions as well (Dickinson and Cicerone, 1986). Biomass contains high amounts of alkali species. In this sense it becomes relevant to study the possible effect of the alkali metals on the formation/reduction of nitrogen oxides (NO_x, N_2O) from combustion systems. Compared with fossil fuels, e.g., coal, biomasses have large amounts of sodium

(Na) and potassium (K), as well as minor amounts of other metals, e.g., magnesium (Mg), manganese (Mn) and iron (Fe).

A practical method to reduce NO_x emissions is the addition of additives to the flue gas. Over the years, several technologies have been developed to study the effects of different compounds, e.g., ammonia and urea (Lyon, 1975; Arand et al., 1980; Schrecebgost et al., 1998). Moreover, it has also been shown that the alkali metals present in the fuel are capable of effectively enhancing the NO_x reduction in staged/non-staged combustion systems (Zamansky et al., 1999; Lissianski et al., 2001; Lee, 2005). The enhancement of the reduction of emissions is a very new topic and complete understanding on the chemistry of Na and K is still a challenge.

In this work, the importance of alkali vapors (K and Na) on gas-phase oxidation of volatile fuel-nitrogen species (NH_3, HCN) to nitrogen oxides (NO_x, N_2O) was studied based on detailed chemical kinetic modeling at ideal reactor conditions and atmospheric pressure using the detailed kinetic modeling package Chemkin 4.0 (Reaction Design, 2004a). The combustion of 2 wood-based biomasses, i.e. wood and bark, in fluidized bed conditions at atmospheric pressure and in the range of temperatures 1073-1473 K and at 3 different staging ratios (SR = 0.7/1.2; 0.9/1.2 and 1.2/1.2) was considered, as well as the combustion of black liquor (spent liquor from pulp production) in recovery boilers under similar conditions. The NO_x emissions were studied to give guidance about optimum conditions in the burning systems while applying staging methods. The purpose of the work was to theoretically describe and understand the effect of the Na and K in relevant industrial conditions in order to help in further improvement of the techniques for efficient NO_x control. Validation of the mechanisms was performed using experimental data from the literature.

Wei et al. (2005) studied the behavior of gaseous chlorine and alkali metals of 3 sorts of biomass by determining the thermodynamic equilibrium concentrations of these biomasses. Their results showed that at temperatures above 1000 K the main potassium species present in the gas phase are KCl and KOH for straw combustion, and KCl, K_2SO_4 and KOH for wood combustion (Wei et al., 2005). Presumably, the same behavior should be expected for the sodium chemistry. In the absence of S and Cl, the major species that should be present from a thermodynamic point of view in the combustion of the wood

and straw is the hydroxide corresponding to the alkali metals (Na and K). Hupa et al. (2001) studied the thermodynamic equilibrium of BL combustion in the temperature range 1073-1473 K. They claimed that in the gas phase the main sodium species are Na and NaOH. In this sense, the assumption of introducing the metal in its hydroxide form was considered appropriate. Moreover, it was expected that the hydroxide species would remain stable when the chemical reactions in the reactor "were completed". This was demonstrated and discussed further in this paper.

Kinetic Scheme and Validation

Kinetic modeling is a valuable tool for predicting and understanding the oxidation and emission-formation mechanisms of combustion processes. The *KILPINEN97* kinetic scheme (Kilpinen, 1997), consisting of 353 reversible gas-phase chemical reactions between 57 chemical species, was completed with 44 more reactions and 10 alkali species (Na and K based) (Glarborg and Marshall, 2005). Two different mechanisms were considered: Mechanism I (MI), without considering the hydrocarbon species of the system, and Mechanism II (MII), including them.

Mechanism I

Zamansky et al. (1999) studied the effect of Na_2CO_3 on NO reduction in a laboratory-scale flow reactor. The experimental setup consisted of a flow system working at atmospheric pressure. A mixture composed of 270 ppm NO, 270 ppm NH_3, 5% O_2 and 8% H_2O in N_2 (as the carrier gas) was introduced into the reactor at 1205 K. The residence time was established to be 200 ms. In the calculations, the Na_2CO_3 was introduced with the feed as NaOH (according to thermodynamic calculations, the sodium carbonate undergoes rapid transformation into sodium hydroxide at that temperature in those kinds of systems). Two different mixing models were considered: ideal and non-ideal mixing. The ideal mixing was described by introducing the NaOH in the feed together with the mixture (instantaneous mixing), while the non-ideal mixing was described by the Curl's mixing model (Janicka et al., 1979) with the specification of a delivery time of 100 ms.

Figure 1 shows a comparison of the experimental data using the 2 models. Both models theoretically described the system very well and the non-ideal delayed mixing gave a better approximation than the

ideal one. This is most probably due to the fact that the experimental conditions are not an ideal plug-flow reactor and the non-instantaneous mixing aspects play an important role. The most obvious result of delayed mixing effects is a somewhat increased NO_x reduction efficiency under these conditions. The error bars are taken as reported in Zamansky et al. (1999).
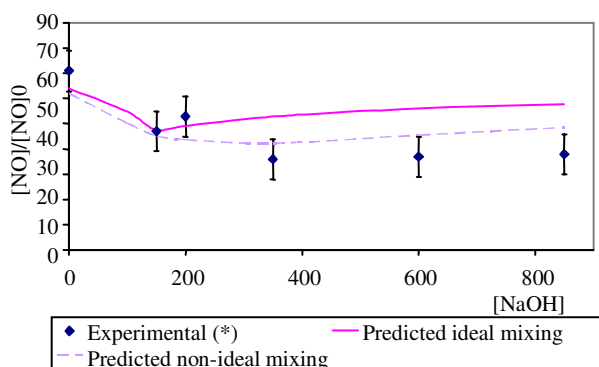

Figure 1. NO removal efficiency (ratio of NO_{out}/NO_{in}) as function of the Na_2CO_3 concentration. Comparison of experimental data (Zamansky et al., 1999) and modeling results: 270 ppm NO, 270 ppm NH_3, 5% O_2 and 8% H_2O in N_2. T = 1205 K, P = 1 atm. Mixing time (non-ideal mixing case) = 100 ms.

Mechanism II

Lissianski et al. (2001) studied the effect of Na and K concentration on NO_x reduction in a boiler simulator facility. The complete description of the experimental system can be found in Zamansky et al. (1999). The simulations were carried out according to the described experimental conditions. The reactor was fed with natural gas as the main fuel, keeping the initial concentration of NO_x at 600 ppm (all the NO_x was introduced as NO). The temperature profile was simulated according to the experimental setup and can be found in Lissianski et al. (2001). The temperature gradient was about -300 K/s, in the range 1800-1200 K. The stoichiometric air/fuel ratio (SR) was set to 1.15.

Figure 2 shows a comparison between the experimental data and the simulation results for the *reburning* and *non-reburning* cases. The results predicted by the model evidenced a clear dependence between the metal concentration and the NO reduction. In both cases, the model overpredicts the NO_x reduction. The experimental results obtained

by Lissianski et al. (2001) showed an optimum at the Na concentration of ca. 500 ppm (see Figure 2), while the modeling predicted a continuously increasing trend. Lee et al. (2005) stated that experiments in similar systems also showed a dependence of NO reduction efficiency with the metal concentration in the fuel. The deviations between the experimental data and the model predictions in the reburning case (Figure 2, bottom) were as small as 1%, with a maximum deviation of 17%. For the case without reburning (Figure 2, top), the model predicted a higher NO_x reduction than the experimental results for different Na concentrations. The overprediction could be explained by mixing effects: the poor mixing in the reactor during the experiments could have caused a lower NO reduction than that predicted with an ideal mixing model, as significant parts of promoters could pass through the reactor untackled with the fuel. From the chemistry point of view, Figure 2 is
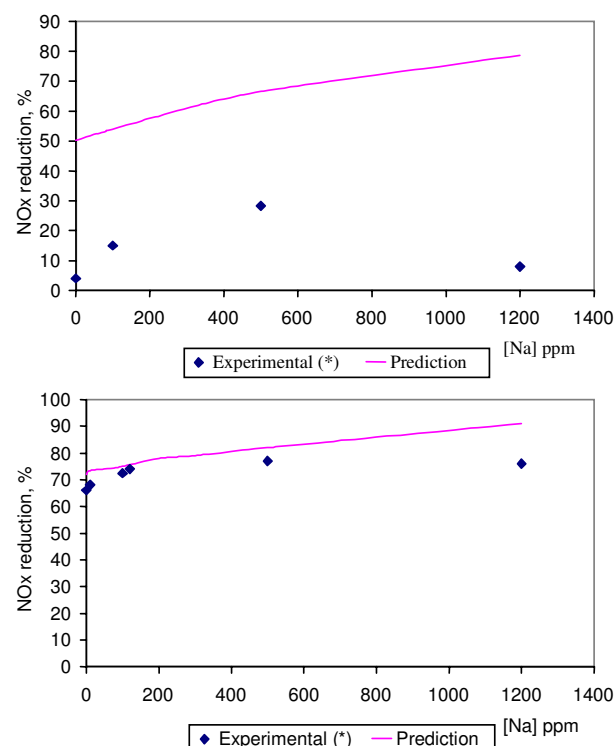

Figure 2. NO_x reduction efficiency as a function of the NaOH concentration. Comparison between experimental data (Lissianski et al., 2001) and modeling results. Promoters injected with the main fuel. $[NO_x]$ = 600 ppm, SR = 1.15. No-reburning case (top). Reburning case, SR_1 = 1.15, SR_2 = 0.86, SR_3 = 1.15, 25% reburning fuel of total heat input (bottom).

different than Figure 1. Figure 2 deals with CH4-ignition chemistry while Figure 1 copes with selective non-catalytic reduction (SNCR) chemistry.

Calculations Procedure

The utilized model for the reactor system is schematically illustrated in Figure 3. All the calculations were carried out assuming a flow of the fuel entering into a plug flow reactor "working" at atmospheric pressure. The reactor was assumed to be isothermal and the temperature range employed for the simulations was 1073-1473 K, which is relevant for combustion of the studied fuels in fluidized beds (wood and straw cases) and recovery boilers (BL case). The total stoichiometric ratio air/fuel (SR) in the combustion zone was set to 1.2 considering 3 staging cases: strong staging SR = 0.7/1.2, normal staging SR = 0.9/1.2, and no staging SR = 1.2/1.2 (direct burning). At time t = 0, the fuel was "injected" together with the air (at SR = 0.7, 0.9 or 1.2, depending on the case). At t = 0.45 s the remaining amount of air in order to reach the SR of 1.2 was "introduced" into the reactor. The total residence time in the reactor was considered to be 1 s. Three different inlet conditions were assumed: no alkali species on the inlet (A case), only NaOH as alkali species on the inlet (B case) and NaOH and KOH as alkali species on the inlet (C case). These conditions were tested with MI, as well as with MII (cases AWCH, BWCH and CWCH).

In order to implement the model in the Chemkin 4.0 kinetic package (Reaction Design, 2004a), 2 batch reactors connected in series were employed (for the cases of strong staging and normal staging). For the first reactor, a residence time of 0.45 s was defined, and, for the second one, a residence time of 0.55 s was utilized. For the case of no staging, the Chemkin configuration consisted only of a batch reactor with a residence time of 1 s. Batch reactors were used instead of plug flow because of the convenience of specifying residence times in the program. The approach was the same as that in the model presented in Figure 3. The air was injected at different SR until reaching the air-to-fuel stoichiometry of 1.2. Ideal mixing was assumed unless specified, and no axial diffusion was considered.

The 3 tested fuels were Finnish black liquor (BL), Danish straw (DS) and Swedish wood (SW). The compositions of DS and SW were taken from the literature (Wei et al., 2005), while the composition of BL was taken from typical compositions in pulp mills (Backman, 1998). In Table 1, these compositions are presented.

Due to the lack of available experimental data, the release factors of the oxygen in the wood and straw were set to 100, and the values of the other compounds were set equal to the value that gives the total volatiles amount, as reported by Wei et al. (2005). The volatiles in percentages as presented in Wei et al. (2005) are 71.32% for DS and 84.10% for SW. In the case of BL, the dry solids content was assumed equal to 70%. All water vapor due to moisture was included in the pyrolysis gases. The elements present in the different fuels were then distributed into the following species: C_2H_4, CO, H_2,
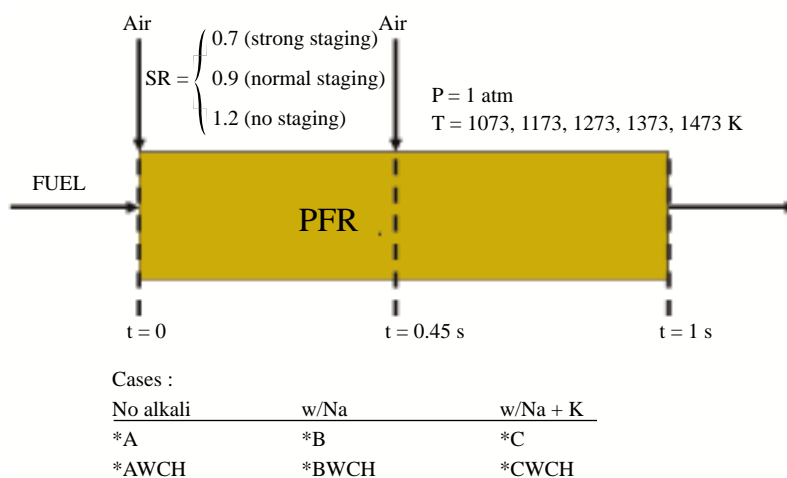

Figure 3. Scheme of the modeling concept.

Table 1. Chemical analysis of the different fuels used.

Fuel →	Black liquor		Danish straw		Swedish wood	
Compound	wt % (dry) [±]	RF [‡]	wt % (dry) [†]	RF	wt % (dry) [†]	RF
C	34.100	50.0	37.528	42.0	45.719	69.8
H	3.400	90.0	9.113	42.0	6.542	69.8
N	0.070	75.0	0.987	42.0	0.065	69.8
Na	22.300	50.0	0.028	42.0	0.003	69.8
K	1.200	50.0	1.318	42.0	0.013	69.8
S	5.530	40.0	0.090	42.0	0.055	69.8
Cl	0.200	50.0	0.481	42.0	0.009	69.8
O	33.20	70.0/40.0*	50.45	100.0	47.59	100.0

†Wei et al., 2005

‡McKeough, 2004

± Backman, 1998

* RF for the case where hydrocarbons were present

H_2O, NH_3, N_2, NaOH, and KOH. The consideration that 50% of the total volatile N goes to NH_3 and the other 50% goes to N_2 has been made (Kymäläinen, 2001). When taking into account the presence of Na and/or K (Cases B and C) this has been done without altering the CO, H_2 and H_2O amounts. The maximum deviation in the O or H balance caused by the assumptions was about 30% -40%. Since this is mainly a qualitative and parametric study, the results were not expected to be dramatically influenced by these assumptions. This conclusion is supported by our earlier experience and results (Kilpinen et al., 1998; Vakkilainen et al., 1998). Keeping the same conditions for all the simulations, an appropriate platform for comparison of the effect of Na and K is established. In this sense, the results of this work could assist in the development of a more complete and accurate model for future calculations.

To calculate the injected air at the 2 different stages, the oxidation reactions of C, H, O, Na and K to CO_2, H_2O, O_2, NaO_2 and KO_2 respectively were considered (Hernández and Kilpinen, 2005).

The necessary oxygen was calculated assuming the concentration of the air to be 79% N_2 and 21% O_2. To study the NO reduction, the N_{fix} reference amount was considered. This value represents the total amount of nitrogen present in the system excluding molecular nitrogen (N_2) with respect to a *reference value* of nitrogen. The *reference value* was taken from the highest studied temperature (1473 K) and no staging case (SR = 1.2). This allows an easier qualitative and quantitative analysis and comparison of the data. In this sense, at the inlet of the reactor, the N_{fix} amount was equal to the NH_3 molar flow,

since this was the only species containing N (besides molecular nitrogen N_2). Sensitivity analysis was also applied to investigate the most crucial reactions in the system.

Results

Black liquor combustion

Effect of temperature, air staging and pyrolysis gas composition The combustion of BL was studied in the range of temperatures of 1073-1473 K. Three different staging ratios were considered (0.7/1.2, 0.9/1.2, and 1.2/1.2). The 2 mechanisms (I and II), and the 3 conditions (A,B, and C) were tested. The simulation matrix for the BL consisted of 90 simulations (5 temperatures, 3 staging ratios, 2 mechanisms and 3 inlet conditions). Figure 4 shows the results of the N_{fix} reduction at the different temperatures for the strong staging case (SR = 0.7/1.2) and the 2 mechanisms. The plot illustrates that the B and C cases (NaOH, and NaOH and KOH, respectively) showed a better N_{fix} reduction than the base case (A case, neither NaOH nor KOH). It appears to be also an optimum in temperature around 1373 K for the MI case, and around 1273 K for the MII case.

In the same way, Figure 5 shows the same results at the normal staging case (SR = 0.9/1.2). The optimum temperature in this case is closer to the 1273 K value for both mechanisms.

Finally, Figure 6 shows the case of no staging (SR = 1.2/1.2). The behavior is similar to that obtained in Figures 4 and 5.
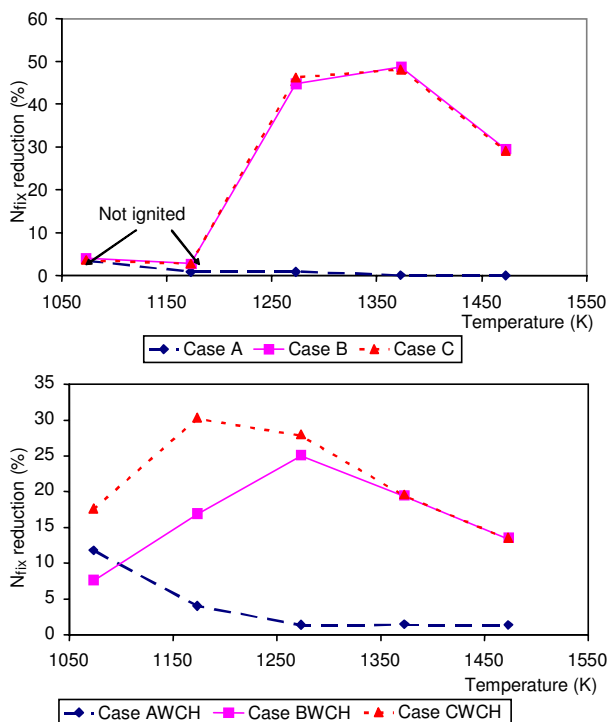
Figure 4. N_{fix} reduction at different temperatures. Combustion of black liquor. SR = 0.7/1.2. Mechanism I, without hydrocarbons. Molar fractions: XCO = 0.13, XH$_2$ = 0.13, XH$_2$O = 0.22, XNH$_3$ = 1.7 * 10^{-4}, XO$_2$ = 0.10, XNaOH = 4.4 * 10^{-2}, XKOH = 1.3 * 10^{-3}, N$_2$ as balance (top). Mechanism II, with hydrocarbons. XC$_2$H$_4$ = 2.6 * 10^{-2}, XCO = 7.4 * 10^{-2}, XH$_2$ = 8.2 * 10^{-2}, XH$_2$O = 0.21, XNH$_3$ = 1.7 * 10^{-4}, XO$_2$= 0.12, XNaOH = 4.3 * 10^{-2}, XKOH = 1.4 * 10^{-3}, N$_2$ as balance (bottom).

A well-established path in the literature for the formation of NO is via NH$_i$. It is also known that it can proceed either towards the formation of N$_2$ (with NH$_i$ and NO as reactants) or towards the formation of NO (with NH$_i$, O and H as reactants). When no alkali compounds are present, no optimum temperature is observable. The radical-pool concentrations are very high in this case, leading to the formation of NO from NH$_i$. When alkali vapors are present, there is a reduction in the radical-pool concentrations. In this case, the NO reduction deals with competition between the 2 possible paths from NH$_i$. At lower temperatures we have probably some of the NH$_i$ left in the system, producing NO and reducing the NO reduction efficiency by alkali species. At higher temperatures, the dominant path is the formation of NO in the competitive reactions. There is a maximum, however, in which the formation of N$_2$ predominates

over the formation of NO, since the radical pool concentration is reduced due to the reactions of the alkali species with them.

It was suspected that at temperatures below 1200 K the reaction system was not ignited, especially for the MI case. Hence, some tests were done with longer residence times in the reactor. These tests are shown in Figure 6, considering residences time of 10 s. With this time, the N_{fix} reduction efficiency grew considerably at lower temperatures, shifting the optimum temperature value to the left part of the curve, i.e. 1173 K for the MI. However, for the MII case, the optimum temperature remained at the same level (around 1273 K). In order to make a proper comparison, the reactor residence time should be kept constant.

The N_{fix} reduction was stronger in the case of MI than in the case of MII. Yet, the trend in both mechanisms was the same, with an optimum temperature for the N_{fix} reduction between 1273 and 1373 K.
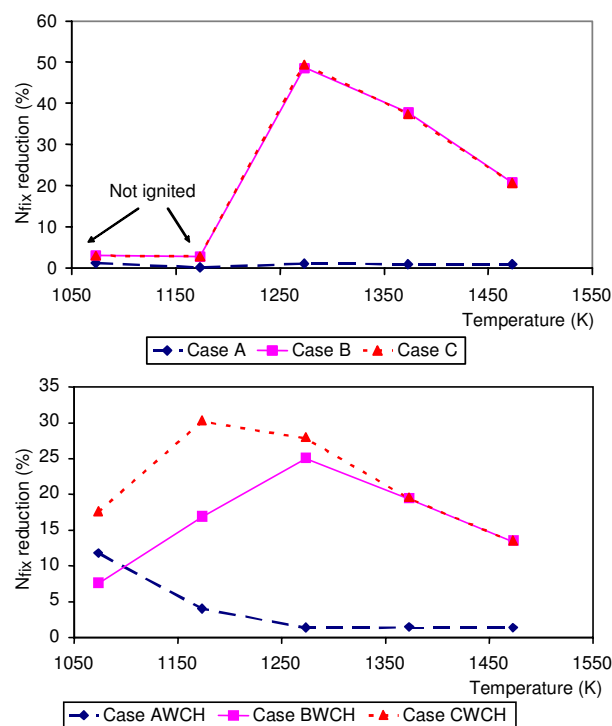

Figure 5. N_{fix} reduction at different temperatures. Combustion of black liquor. SR = 0.9/1.2. Mechanism I, without hydrocarbons (top). Mechanism II, with hydrocarbons (bottom).
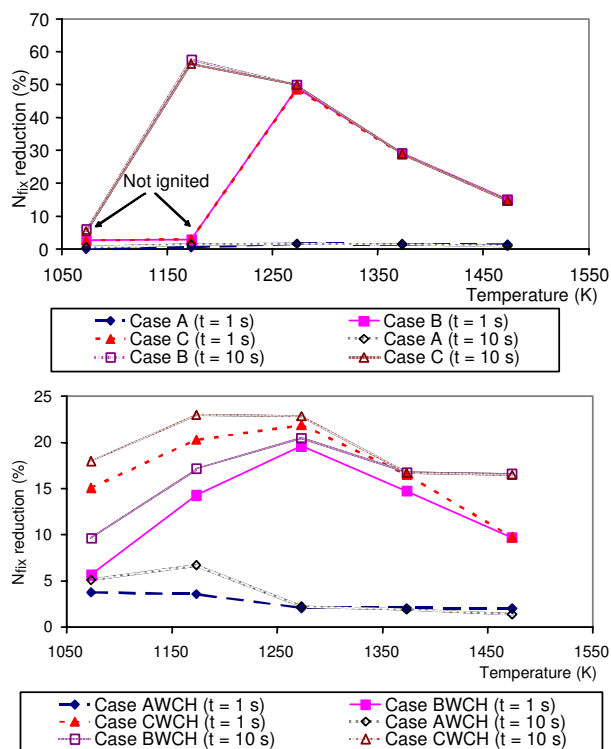
Figure 6. N_{fix} reduction at different temperatures. Combustion of black liquor. SR = 1.2/1.2. Mechanism I, without hydrocarbons (top). Mechanism II, with hydrocarbons (bottom).

Form of Nvol: Replacing NH_3 with HCN or NO/NH_3 mixture In order to determine the influence of the inlet source of NO_x in the reduction of the nitrogen oxides, some tests were carried out changing the inlet concentration of NH_3 for HCN. The results showed that the optimum temperature was shifted toward higher values, in comparison to the NH_3 in the inlet case. This behavior could be explained by the oxidation of HCN to NO being slower than the oxidation of NH_3. Thus, higher temperatures are needed for the reactions to proceed accordingly. Still, the maximum level of reduction was predicted about the same for both systems (around 50%).

To continue with the same kinds of tests, the inlet concentration of NH_3 was divided equally into 2 species: NH_3 and NO. The trend of these results was similar to the NH_3-only case, but the N_{fix} reduction was lower. In fact, the presence of NO does not help to reduce the NO_x further. It was shown in Zamansky et al. (1996) that the presence of NH_3 enhances the NO_x reduction in combustion processes.

Danish straw and Swedish wood combustion

Effect of temperature, air staging and pyrolysis gas composition In these cases, the effect of the alkali compounds was not as significant as in the BL case. However, the alkali vapors chemistry seemed to influence the behavior of the combustion system, especially at lower temperatures. In the case of no staging (SR = 1.2), the C case (Na and K present) showed a better N_{fix} reduction. In the best case for DS, the difference reached 17% more of the N_{fix} reduction than the base case (A case, neither Na nor K). The results also indicated that the alkali compounds present in the SW do not strongly influence the behavior of the combustion system. The trend of the N_{fix} reduction was the same as that observed in the combustion of DS. Because of the small amounts of alkali species present in this fuel, it was difficult to observe a difference between the 3 tested cases (A, B and C). The reductions of N_{fix} were also smaller for the SW (maximum value of 25%) than in the DS (max. 45%) and BL (max. 50%). SW has practically no Na (see Table 1), which explains why the results in the A and B cases were very similar.

Effect of Na and K concentration in NO reduction The outcome of the simulations demonstrated that the chemistry of Na and K has an important effect on the combustion of different types of fuels. The employed model predicted an enhancement of the N_{fix} reduction efficiency when the metals were present in their hydroxide form. Consequently, the effect of the metal concentration in the system was then studied for the combustion of BL. The simulations were carried out at 1373 K, and the concentration of the alkali metal (in hydroxide form) was varied from 0 to 400,000 ppm (an unrealistic value in a fuel, but used for observing the trend). Two different staging conditions were considered (SR = 0.7/1.2 and SR = 1.2/1.2). Figure 7 describes the performance of the system at different Na and K (as NaOH and KOH respectively) concentrations.

It appears, especially for Na, that a maximum amount of the metal influences the system (or does not change considerably the NO reduction), which is roughly X = 0.05 (as molar fraction). It is also shown in Figure 7 that the case of strong staging was capable of enhancing the NO reduction more than was the case of no staging. This behavior was observed with the other 2 studied fuels as well.

Potassium appeared to have less influence than sodium in the studied system. Similar behavior was

found experimentally in Zamansky et al. (1996). It can be seen from the same figure that in the studied concentration range of potassium the increase in the NO reduction was steady, even at very large concentrations of the metal hydroxide (>200,000 ppm).
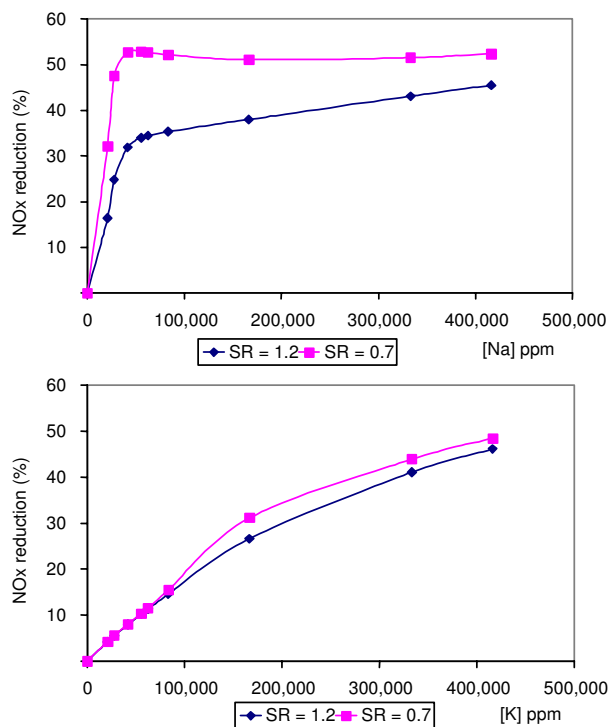

Figure 7. Effect of the metal (as MOH) concentration on the NO reduction efficiency. Combustion of black liquor, Mechanism I, Temperature = 1373 K. M = Na (top). M = K (bottom).

Chemical reaction path analyses

Figures 8-10 depict the concentration profile in the reaction system for the sodium-containing species in logarithmic scale at different temperatures and staging conditions (SR = 0.7/1.2 -top- and SR = 1.2/1.2 -bottom-). It is possible to deduce together with a mechanistic analysis the different reaction paths that the Na-containing species follow. Figure 11 shows a simplified scheme of the pathway of the Na (top) and K (bottom) species. In the case of Na chemistry, the most stable species were found to be $Na_2O_2H_2$, NaO_2, and NaOH and Na. At higher temperatures, i.e. over 1350 K, almost all the sodium existed as $Na_2O_2H_2$ and NaOH. The tendency was rather similar in the K case. However, KO was found to be more stable than the K at the end of the residence

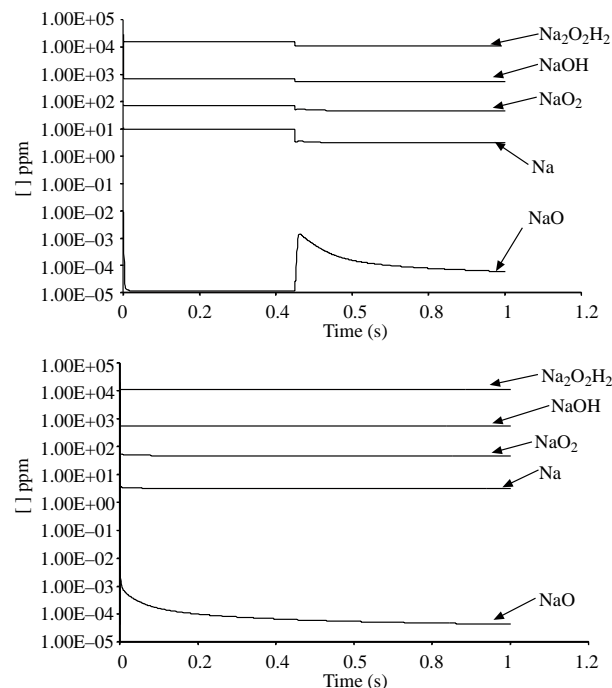time, the opposite of what was observed in the Na (see Figure 11 top).

Figure 8. Sodium-containing species concentration vs. reactor time. T = 1073 K, Mechanism I. SR = 0.7/1.2 (top) and SR = 1.2/1.2 (bottom).

The presence of alkali vapors tends to reduce the radical pool in the system. In this sense, the Na and K present "remove" the active oxidation species OH and O and hence reduce the formation of NO. This same behavior was encountered experimentally and discussed using modeling in Zamansky et al. (1999).

The results showed that the reaction path of the sodium was NaOH→ Na→ NaO$_2$ → NaO→ NaOH (see Figure 11, top). Perry and Miller (1996) found that the reaction path of Na leading to the control of nitrous oxide reduction was NaOH→Na→NaO→NaOH, being the net effect of the destruction of N_2O molecules. They claimed that the behavior of other alkali metals, i.e. K, was the same. Therefore, the alkali metals enhance the NO_x, as well as the N_2O reduction in the combustion systems studied.

Calculations were also carried out without considering the reaction MOH+MOH→$M_2O_2H_2$ (where M represents either Na or K) in the mechanisms. The effects were the same as those presented in Figure 11, without the mentioned compound in each of the schemes.
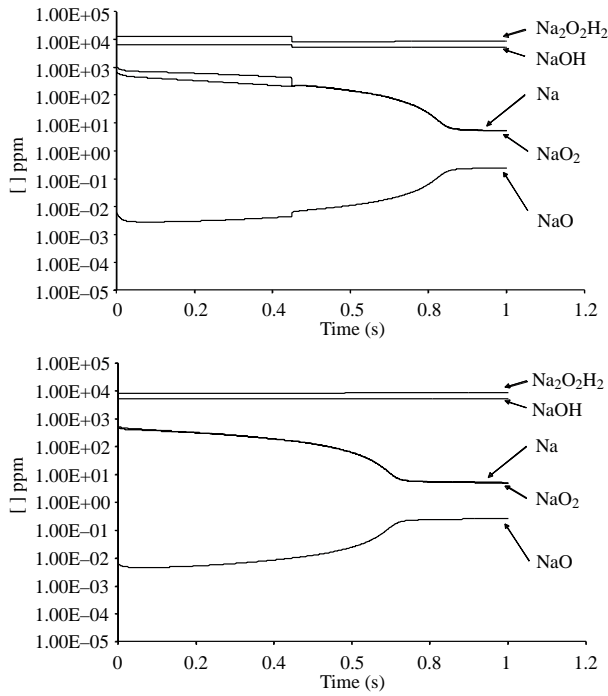
Figure 9. Sodium-containing species concentration vs. reactor time. T = 1273 K, Mechanism I. SR = 0.7/1.2 (top) and SR = 1.2/1.2 (bottom).
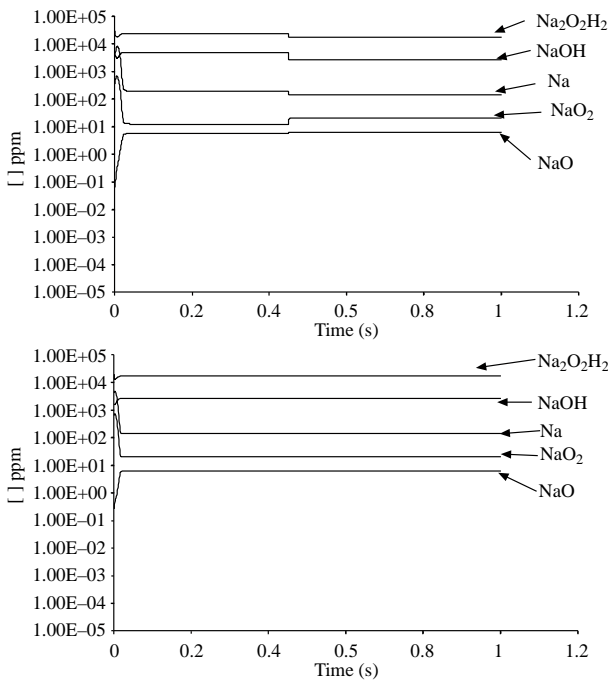

Figure 10. Sodium-containing species concentration vs. reactor time. T = 1473 K, Mechanism I. SR = 0.7/1.2 (top) and SR = 1.2/1.2 (bottom).
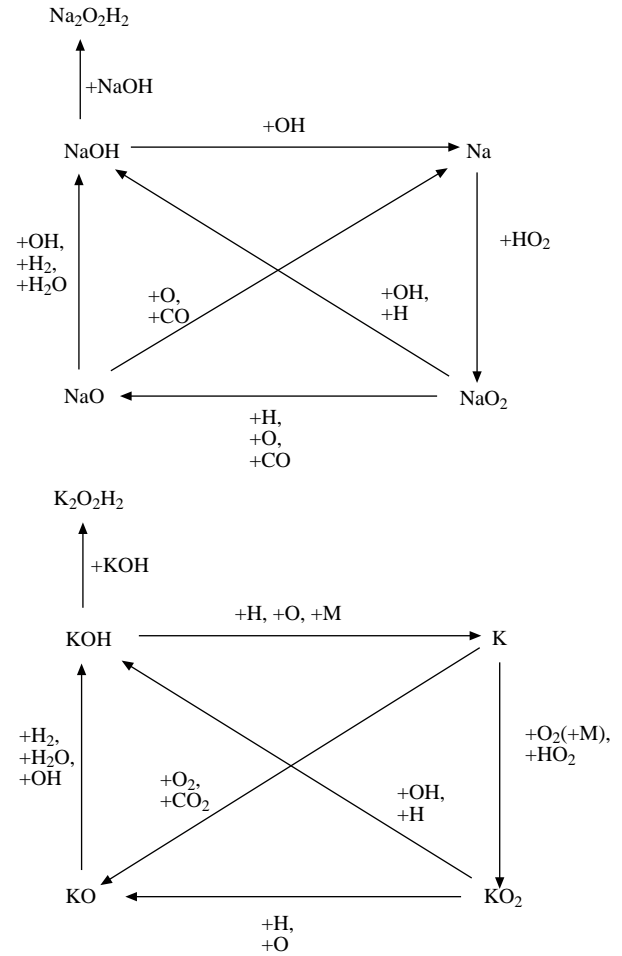

Figure 11. Diagram of the sodium-containing (top) and the potassium containing species (bottom) and their reactions.

Sensitivity analyses

In order to study the effect of the uncertainty of the reaction-rate constants, sensitivity analysis was applied. The Chemkin capabilities were used for this purpose (Reaction Design, 2004b). Strong staging and no staging conditions were tested at T = 1373 K for the combustion of BL. Figure 12 shows the behavior of some of the N-containing species present in the system in logarithmic scale (top) as well as the sensitivity analyses for NO (bottom). Because of the large number of reactions present in the system, the cut-off values in the figure for all the reactions except the alkali ones were set to 0.2 (bottom left), while for the sodium chemistry reactions this value was set to 0.5 (bottom right). After the residence time of t = 0.3 s, no reactions were sensitive; hence, this part of the plot is not shown (Figure 12, bottom).

Table 2. Most sensitive reactions in the system.

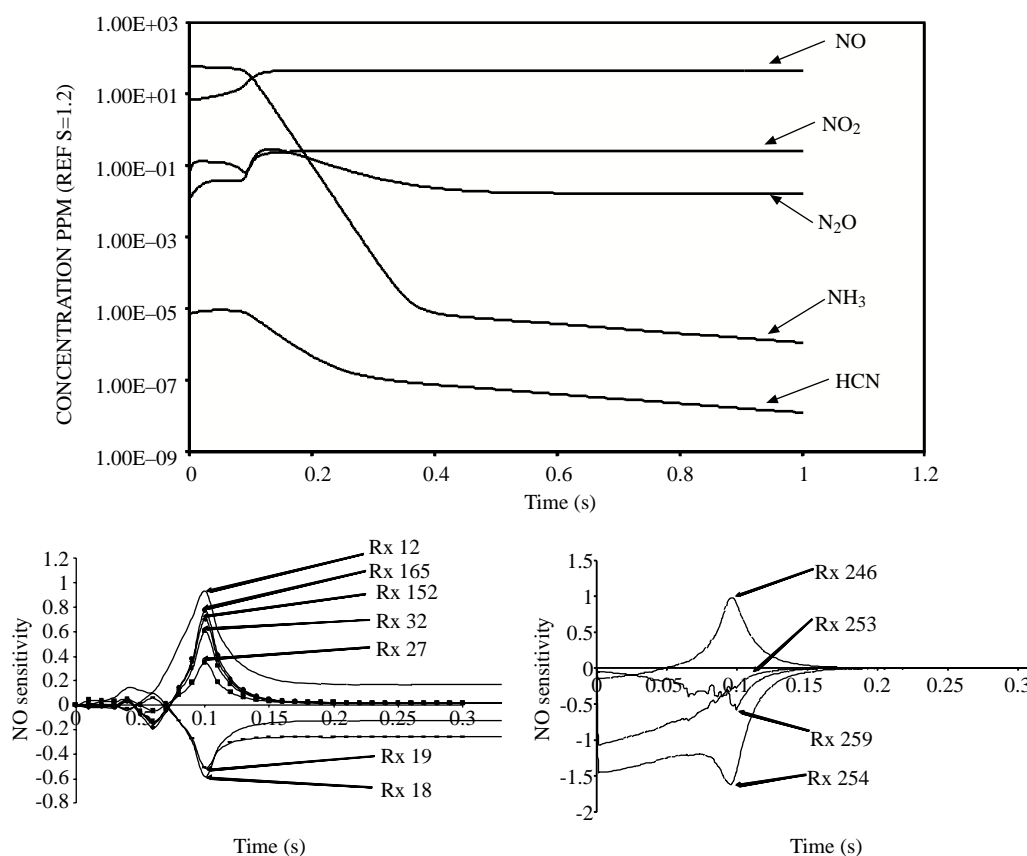|			
$H_2NO + O \rightarrow NH_2 + O_2$	{R12}	$HNCO + M \rightarrow CO + NH + M$	{R165}
$NH_2 + NO \rightarrow NNH + OH$	{R18}	$NaO + O \rightarrow Na + O_2$	{R246}
$NH_2 + NO \rightarrow N_2 + H_2O$	{R19}	$NaO + CO \rightarrow Na + CO_2$	{R253}
$NH + O_2 \rightarrow HNO + O$	{R27}	$NaOH + H \rightarrow Na + H_2O$	{R254}
$NH + NO \rightarrow N_2O + H$	{R32}	$NaO_2 + O \rightarrow NaO + O_2$	{R259}
$NCN + O_2 \rightarrow NO + NCO$	{R152}	$NaO_2 + OH \rightarrow NaOH + O_2$	{R260}

Figure 12. N-containing species concentration vs. reactor time (upper) and sensitivity analyses for NO. Combustion of black liquor, Mechanism I, SR = 1.2/1.2. T = 1373 K. All reactions but alkali ones, cut-off value 0.2 (lower left). Sodium-species reactions, cut-off value 0.5 (lower right).

The reactions identified as the most sensitive in the spectrum are presented in Table 2 (numbers in braces indicate the reaction number in the mechanism).

Conclusions

Under the conditions studied, the alkali vapors showed a clear enhancement effect on the N_{fix} and NO_x reduction efficiency. The optimum temperature was between 1273 and 1373 K, obtaining a NO_x reduction efficiency of ca. 50%.

It was stated that at higher alkali-metal concentrations, the enhancement of NO_x reduction was also higher, obtaining the best results for the Finnish black liquor, followed by the Danish straw, with the lowest improvement in NO reduction in the Swedish wood.

When hydrocarbons were present in the system, the prediction of the NO_x reduction efficiencies were lower than in the case without hydrocarbons. Under the conditions studied, most of the NO_x in the outlet was represented by NO. Within the temperature range studied, the N_2O, NO_2, and NO_3 amounts in the system were minimal.

The use of HCN instead of NH_3 in the inlet led to lower NO_x reduction. This was attributed to the slower oxidation of this species (HCN) under the conditions studied.

The addition of potassium, even if it showed an improvement in the NO_x reduction efficiency, was lower than in the case of sodium.

Further development of the model of the alkali species is needed. More comparisons with available experimental results of other combustion systems are necessary in order to definitely validate the model.

Acknowledgments

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