Reburning in Oxy-Fuel Combustion: a Parametric Study of the Combustion Chemistry

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Abstract

The present work investigates reburning reduction of nitrogen oxides in oxy-fuel combustion by means of a detailed reaction mechanism applied to a plug-flow reactor. Reburning reactions, which are known to convert NO_x into N_2, are of special interest in oxy-fuel combustion due to extensive recirculation of flue gases, including NO_x, to the flame. Furthermore, the high concentration of carbon dioxide in oxy-fuel combustion is known to influence the radical pool (H/O/OH), which is critical to the combustion chemistry. In the present work it is shown how the changes in the radical pool alter the nitrogen chemistry both directly and indirectly by influencing the formation and oxidation of hydrocarbon radicals. It is shown that reburning is more sensitive to the combustion temperature but less affected by the combustion stoichiometry under oxy-fuel compared to air conditions. The main reasons are the impact of increased CO_2 concentration on hydrocarbon oxidation and the increased importance of CH_3 as a reactant in oxy-fuel combustion.

Keywords: Oxy-fuel combustion, Reburning, Nitrogen oxides

Introduction

In oxy-fuel combustion, oxygen (O_2) diluted by a certain amount of recirculated flue gas is introduced into the furnace to burn the fuel and to produce a flue gas highly concentrated in carbon dioxide (CO_2). The amount of recirculated flue gas is chosen to achieve the desired flame temperature. The primary objective for developing oxy-fuel combustion is to capture CO_2, but the technique also implies new options for control of nitrogen oxides (NO_x)[1]. However, most of these options require further exploration in order to optimize oxy-fuel power plants. The present work focuses on reburning of NO_x. Reburning (or fuel staging) was proposed for NO_x control in pulverized-fuel combustion in 1973[2] and has been thoroughly investigated for air-fired applications[3-5]. The objective of reburning is to create hydrocarbon radicals (CH_i), which can reduce NO_x to N_2. A reburning process consists of a reburn zone and a burnout zone. The reburn zone should be oxygen lean to promote formation of radicals. In the burnout zone, oxygen is added in sufficient amount to complete combustion.

In application of reburning to air-firing, the primary combustion-zone is the source of NO_x and a secondary fuel-stream is supplied to create the reburn zone. In the oxy-fuel application, NO_x is instead supplied by the recirculated flue gas and the primary combustion forms the reburn zone. Typically, recirculation of NO_x into the oxy-fuel flame lowers the emission by around 70% per unit of fuel supplied compared to the emission from air-firing under otherwise similar conditions[1].

The influence of oxy-fuel conditions and especially high concentration of CO_2 on combustion and gas-phase nitrogen-chemistry has been investigated recently. Park et al.[6] observed differences in reaction routes between combustion with high and low CO_2 content in a numerical study. Glarborg and co-workers[7-9] compared experiments in a lab-scale flow-reactor with detailed chemical-kinetic modeling of the gas-phase reactions. When substituting N_2 with CO_2 in the oxidizer, they detected increased formation, but similar reduction of nitric oxide (NO) under oxygen-lean conditions, while the reduction of NO was higher and the formation lower under stoichiometric and oxygen-rich conditions. A similar investigation by Giménez-López et al.[10] concludes that the oxidation of hydrogen cyanide (HCN) forms less NO under oxy-fuel conditions due to the influence of CO_2 on the radical pool. Mackrory[11] investigated the influence of oxy-fuel combustion on nitrogen chemistry by experiments in a pulverized coal-fired reactor and by a model based on established sub-models. He found that the reduction of NO_x in oxy-firing is less sensitive to stoichiometric ratio than in air-firing.

Literature also presents a series of experimental investigations on the influence of combustion parameters (stoichiometric ratio[8-9, 11-14], inlet oxygen concentration[13, 15] and temperature[13]) on NO_x emission. Recent work by Kühnemuth et al.[13] examines the influence of combustion parameters on reburning during oxy-fuel conditions by experiments with propane and reaction modeling. It is concluded that temperature and stoichiometric ratio are crucial parameters for efficient reduction by reburning (both should be kept low), while the direct effect of inlet oxygen concentration is negligible.

As discussed above, the literature presents two types of investigations on reburning reduction of NO_x under oxy-fuel conditions: studies of the chemical reactions in combustion atmospheres with high CO_2 concentration, and studies on differences in the influence of combustion parameters on reburning reduction of NO_x in air and oxy-fuel combustion. The present work aims at complementing these two types of investigation. Here, the gas-phase reburning chemistry related to the sensitivity to certain combustion parameters under oxy-fuel conditions will be closely examined. There are processes besides the gas-phase chemistry, such as mixing and heterogeneous reactions, that should be included in a complete description of the combustion process. However, due to the critical role of the gas-phase chemistry to the NO_x reduction, it is important to investigate it separately; in the present work the reduction potential by homogeneous chemistry is effectively isolated from other mechanisms. The main focus is on the key differences between oxy-fuel combustion and the established reburning process in air combustion. The critical reaction paths in reburning are presented and the differences in sensitivity to temperature, stoichiometric ratio, residence time, and concentration of oxygen in the oxidizer are analyzed. Major differences in the combustion chemistry are also highlighted due to their significance to the reburning process.

Method

The combustion and reburning processes are simulated by a detailed gas-phase kinetic reaction mechanism[8]. A mixture of fuel, oxidizer, and NO, heavily diluted by CO_2 or/and N_2 (the concentrations of $CO_2 + N_2 > 99\%$), is introduced to a plug-flow reactor to simulate a reburning environment instead of involving an entire flame and, thereby, having to deal with boiler geometry and mixing, which are important for the reburning process[16]. The initial concentration of NO is 500 ppm. The fuel is represented by methane, which is a simple and well-documented hydrocarbon, a useful approach when modeling NO_x chemistry. Secondary oxygen is introduced as pure O_2. The mechanism of Mendiara and Glarborg[8] has been validated for oxy-fuel conditions. It includes reactions of importance for combustion of light hydrocarbons and for the complete homogeneous nitrogen chemistry, related to reburning. The mechanism is implemented in the Chemkin-Pro[17] software. The hydrocarbon oxidation and the nitrogen chemistry are evaluated by a reaction-path analysis, performed by calculating the elemental flux of atom A from species i to species j according to

$$\dot{\mathrm{A}}_{ij} = \int_{\mathrm{t}_1}^{\mathrm{t}_2} \sum_{k=1}^{\mathrm{N_R}} \mathrm{q}_k(\mathrm{t}) \mathrm{N}_{\mathrm{A},k}\, \mathrm{dt} \qquad (1)$$

The instantaneous rate of reaction q_k (mol m^{-3} s^{-1}) for every forward and reverse reaction k between species i and j is summarized and integrated between the reaction times t_1 and t_2. In this way, the major paths through the combustion process can be identified. N_R is the number of reactions with reactant or product i and j. $N_{A,k}$ denotes the number of atom A in reaction k. Furthermore, the relative importance of each reaction q_k to the elemental flux is analyzed.

Throughout this work, the combustion process is divided into three stages, I-III, related to the progress of the combustion chemistry, as defined in Fig. 1. Stage I is dominated by hydrocarbon oxidation and is defined as the time between inlet and the peak in CO concentration. The time when secondary oxygen injection takes place defines the end of Stage II. Stage III is the burn-out zone. Thus, the reburn zone consists of Stages I and II.

In the first part of the investigation (the reference case), combustion chemistry with respect to hydrocarbon oxidation and nitrogen chemistry is studied, and the reaction routes of reburning are discussed. This part focuses on the effects of the high CO_2 concentration during oxy-fuel combustion. Replacement of N_2 with CO_2 is the only parameter change made between the air and the oxy-fuel case in the reference calculation: the temperature is 1673K, the O_2-CO_2 ratio (molar) is 0.004, and the stoichiometric oxygen-fuel ratio is 0.7 in the reburn zone (λ_{RB}) and 1.2 in the burn-out zone (λ_{BO}). The simulations are isothermal and thereby the influence of temperature variations when changing inlet composition is eliminated. The time when secondary oxygen is injected (τ_{II}) is not fixed in the reference case. Instead, the ideal occasion for injection is calculated to take place after the time required (τ_{II}') for oxidation of 99% of the HCN peak concentration. Thus, the time required for optimum reduction under oxygen-lean conditions is indicated by τ_{II}'.

The second part of the work investigates the influence of common combustion parameters on reburning during operation with high CO_2 concentration. The temperature is varied from 1100K to 2000K and the stoichiometric ratio (λ_{RB}) from 0.7 to 1.2, independent of each other; one is kept constant as in the reference case, while the other is varied. The influence of residence time in the reburn zone is studied by fixing the time for secondary oxygen injection and by relating the decrease in reduction to the ideal reduction (i.e. if $\tau_{II} < \tau_{II}'$). Again, the influence of combustion parameters in oxy-fuel operation is compared to the corresponding situation

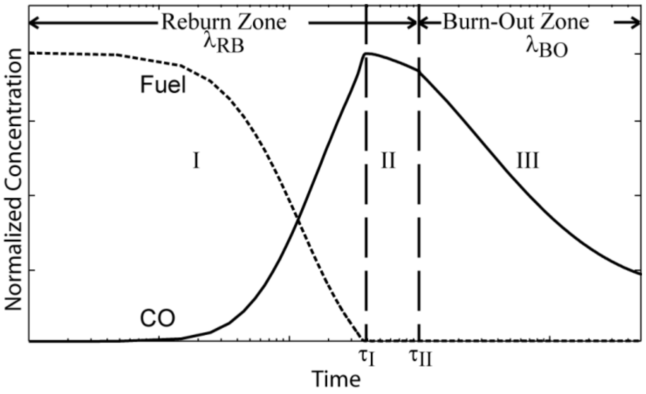

Figure 1. Definition of the three stages of the combustion process during reburning (I, II, and III). Dashed vertical lines indicate the time limit for each stage and arrows denote zones with different stoichiometric ratios (λ).

during air-firing. Finally, the oxygen concentration (O_2-CO_2 ratio) in the modeled flame zone is varied to observe its influence on the results.

Reburning Chemistry

The influence of nitrogen chemistry on combustion is negligible, whereas changes in hydrocarbon oxidation can have a large impact on nitrogen chemistry. Besides the reduction of NO_x by CH_i, hydrocarbon and nitrogen chemistry are connected through the important radical pool of atomic oxygen (O), hydrogen (H), and the hydroxyl radical (OH). This section introduces the chemistry of hydrocarbon oxidation and nitrogen chemistry of importance to the reburning process; the focus is on differences between oxy-fuel and air-fuel conditions.

1. Hydrocarbon Oxidation

The single most important reaction in a combustion process is the chain-branching reaction[18],

$$H + O_2 \rightarrow OH + O \qquad (2)$$

Consequently, production of H-atoms promotes combustion, while consumption of H-atoms inhibits combustion. Reaction (3) produces most of the CO_2 in combustion and is also a key reaction[18].

$$CO + OH \leftrightarrow CO_2 + H \qquad (3)$$

The oxidation of CO in Reaction (3) produces H-atoms and is therefore important for Reaction (2).

In Stage I (Fig. 1) the fuel is oxidized and a high concentration of hydrocarbon radicals is produced. The reaction of hydrocarbon radicals with both H and OH is generally faster than Reactions (2) and (3)[18]. This leads to an accumulation of CO, which starts to oxidize when the hydrocarbon oxidation is completed. It has been concluded in previous studies[19] that the elevated concentration of CO_2 of an oxy-fuel flame forces Reaction (3) in the reverse direction. Figure 2 shows the difference in concentration of chain-carrying radicals between air and oxy-fuel combustion due to the elevated CO_2 concentration of oxy-fuel combustion. The reversed Reaction (3) competes with the reactions between O_2 and H-radicals and may therefore have an impact on flame propagation. The effect is seen in Fig. 2 by the slower oxidation of the fuel during oxy-fuel combustion than during air combustion (Stage I is shorter in air combustion).

In Stage II, when CO starts to oxidize to CO_2 (the forward Reaction (3)) the higher CO concentration in oxy-fuel combustion reduces the relative rate of consumption of radicals and, eventually, the concentration of

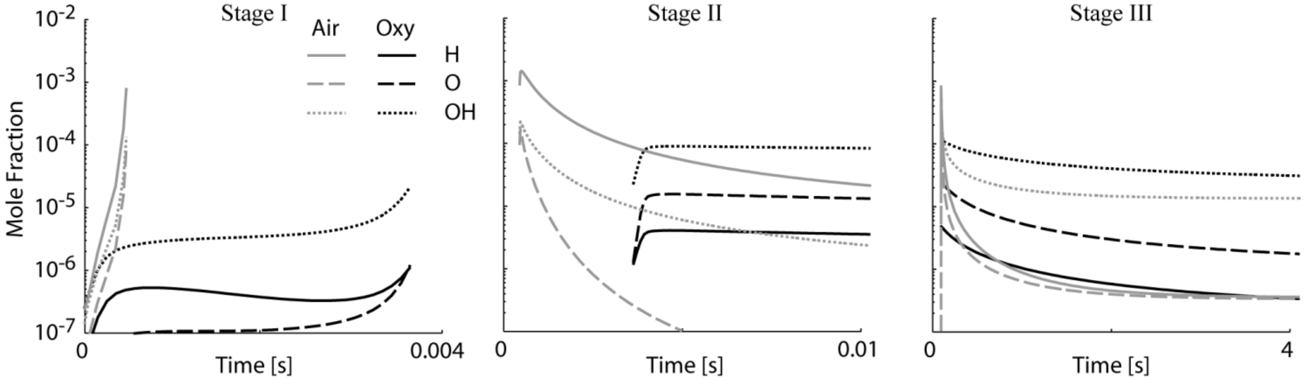

Figure 2. The concentration profile of chain-carrying radicals in the three stages (I, II and III) of the combustion process during air and oxy-fuel condition. Note the different time scales.

radicals in oxy-fuel combustion will exceed that of air combustion, which is seen in the center diagram of Fig. 2. The relative order of the quantity of radicals is changed from H>OH>O in air combustion to OH>O>H in oxy-fuel combustion. When entering Stage III more oxygen is added to complete the oxidation and a similar pattern as in the reburn zone is detected: initially, the concentration of radicals is higher during air-firing, but the decrease is slower during oxy-fuel combustion due to the buffering effect by CO_2 in Reaction (3).

The oxidation of methane can follow the three major routes presented in Fig. 3: two C1 routes through CH_2O or CH_2 and a C2 route through the recombination of CH_3. Since the reduction of NO_x by reburning depends on hydrocarbon radicals, the oxidation of CH_3 is critical. Figure 4 shows the concentrations in the reburn zone (Stages I and II) of CH_3, the sum of CH_2 and CH, and HCCO, which are the most important reducing agents for NO_x. There are important differences in the oxidation of hydrocarbons under air and oxy-fuel conditions. The importance of the reactants in the two cases is indicated by the integration of the concentration in Fig. 4 whose area represents the presence of species over time. The peak concentration of CH_3 is similar in both cases, but the residence time in oxy-fuel combustion is longer. For CH_3, the integrated area is about three times as large

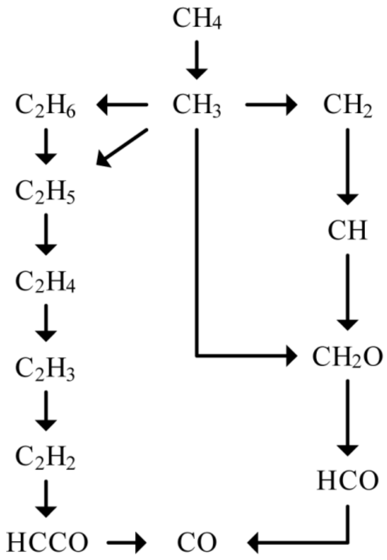

Figure 3. The major oxidation routes of methane.

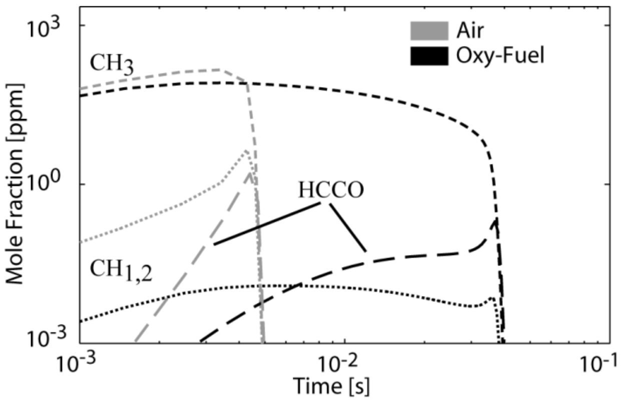

Figure 4. Concentration profile of CH_3, $CH_{1,2}$ and HCCO in air and oxy-firing with the same oxygen concentration. Temperature = 1673K and $\lambda_{RB} = 0.7$.

under oxy-fuel conditions. On the other hand, the peak in $CH_{1,2}$ is almost 500 times lower and the integrated area almost 15 times lower in oxy-fuel combustion. The C1 routes depend more on the chain-carrying radicals than the C2 route. Therefore, the C2 route is less affected by oxy-fuel combustion; the ratio in the integrated total amount of HCCO is 1.5 between oxy and air-firing. The consequence with respect to nitrogen chemistry is that, compared with air firing, the importance of CH_3 is enhanced relative to $CH_{1,2}$ as a reducing agent under oxy-fuel conditions.

2. Nitrogen Chemistry

Figure 5 shows the presence of nitrogen species (except N_2) in the reburn zone (Stages I and II). The progress of NO_x reduction is indicated in Fig. 5a by the concentration of NO and HCN, while Fig. 5b shows the maximum concentration of the common intermediate nitrogen species. HCN is the dominant intermediate nitrogen species, and most of the other common species are related to its formation and oxidation. The peak in NH_3 is about 100 times lower than the peak in HCN under air conditions and about 500 times lower under oxy-fuel conditions. The reduction rate is lower during oxy-fuel combustion, which is seen by the slower increase of HCN in Fig. 5a, due to the lower concentration of hydrocarbon radicals ($CH_{1\text{-}3}$). This is, however, compensated

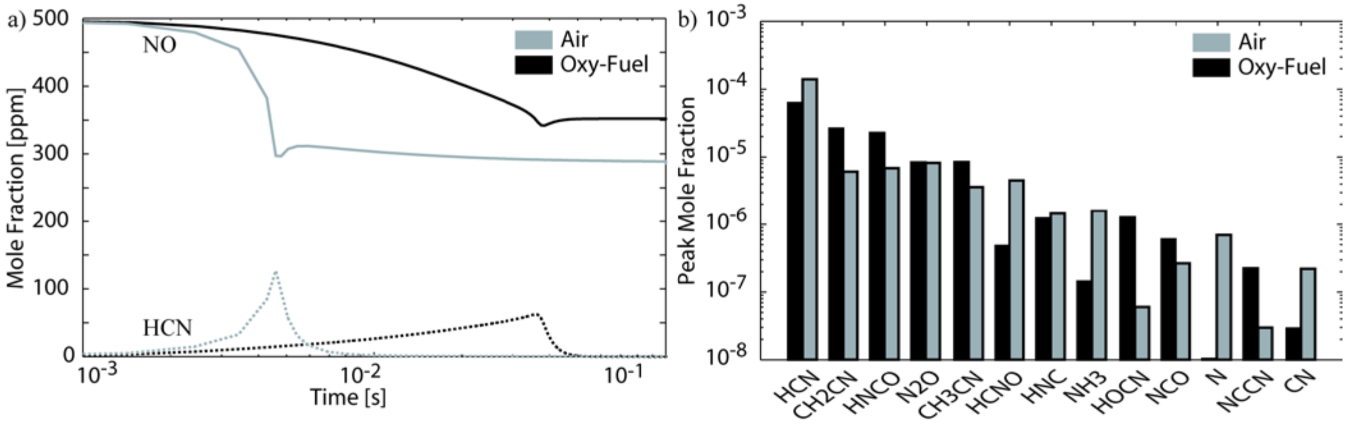

Figure 5. Concentration profile of NO and HCN, in air and oxy-firing with the same oxygen concentration. Temperature = 1673K and $\lambda_{RB} = 0.7$.

by a longer residence time in the reducing zone (Stage I), owing to the slower oxidation of the fuel, which opens up a possibility for alternative reaction routes. Although there are large differences in combustion conditions and in reduction rate between air and oxy-fuel combustion in the investigated cases, the difference in overall reduction of NO is not large (the reduction is around 30% for oxy-fuel and around 40% for air combustion).

Figure 6 shows the governing reaction routes for nitrogen compounds in Stages I and II during air and oxy-fuel combustion. In Stage I the reduction of NO to HCN dominates nitrogen chemistry. In oxy-fuel combustion less HCN is formed directly from NO, mainly due to lower concentration of $CH_{1,2}$. However, this is compensated by enhanced formation of HCN via H_2CN due to higher CH_3 concentration.

In Stage II, HCN and CN react mainly to NCO. In oxy-fuel combustion a route to NCO via a reactive isomer produced through a third-body reaction with H_2O and CO_2 compensates for the lower direct oxidation by O radicals. In air-firing almost all NCO is introduced through a reaction with H-radicals to the amine pool (this route is active already in Stage I), from which either NO or N_2 is formed. In oxy-combustion the concentration of H-radicals is lower, and NCO reacts through alternative paths to form N_2O, NO and N_2. The split between NO and N_2 depends on similar reactants in both cases (NO yields $N_{2,}$ and, OH, O_2 or O yield NO). To summarize, the changes in the radical pool composition in oxy-fuel combustion affect nitrogen chemistry both directly during the oxidation of the intermediate nitrogen species and indirectly via the influence on hydrocarbon oxidation during the reduction of NO_x.

Analysis of the Influence of Combustion Parameters

A parameter study has been performed involving temperature, stoichiometric ratio and residence time. Figure 7 shows the sensitivity of NO reduction to these combustion parameters. Two characteristics are compared to evaluate the performance of the reburning reduction: the minimum NO concentration (normalized) in the gas

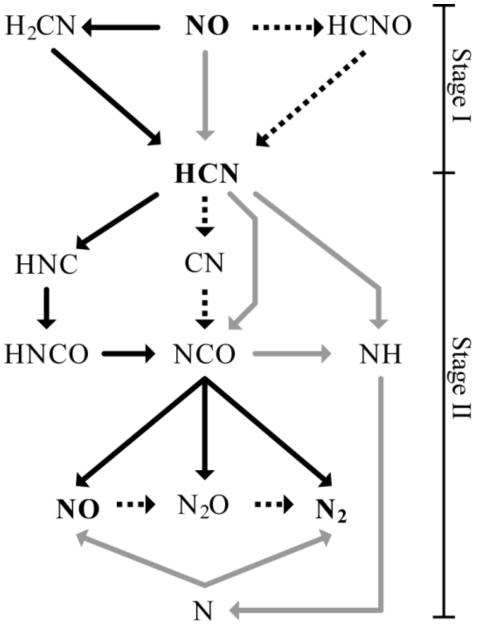

Figure 6. The most important reaction routes in the reburning zone. Black arrows symbolize routes of higher importance for oxy-fuel combustion compared to air-firing, while grey arrows are of lower importance. Dashed arrows are of similar importance in both cases.

leaving Stage I, and the required residence time of Stage I to reach the minimum NO concentration. Figure 7a and 7b show the influence of temperature and stoichiometric ratio respectively, while Fig. 7c illustrates the relative increase of the emissions shown in Fig. 7a (for three temperatures) if the actual residence time (τ_{II}) is less than the required time for maximum reduction ($\tau_{II}´$). In the following sections the implications of Fig. 7 are discussed and the chemistry responsible for the differences between air and oxy-fuel firing is analyzed. Furthermore, the assumption of having the same oxygen concentration in air and oxy-fuel simulations and the influence of flue gas recycling in oxy-fuel combustion are discussed.

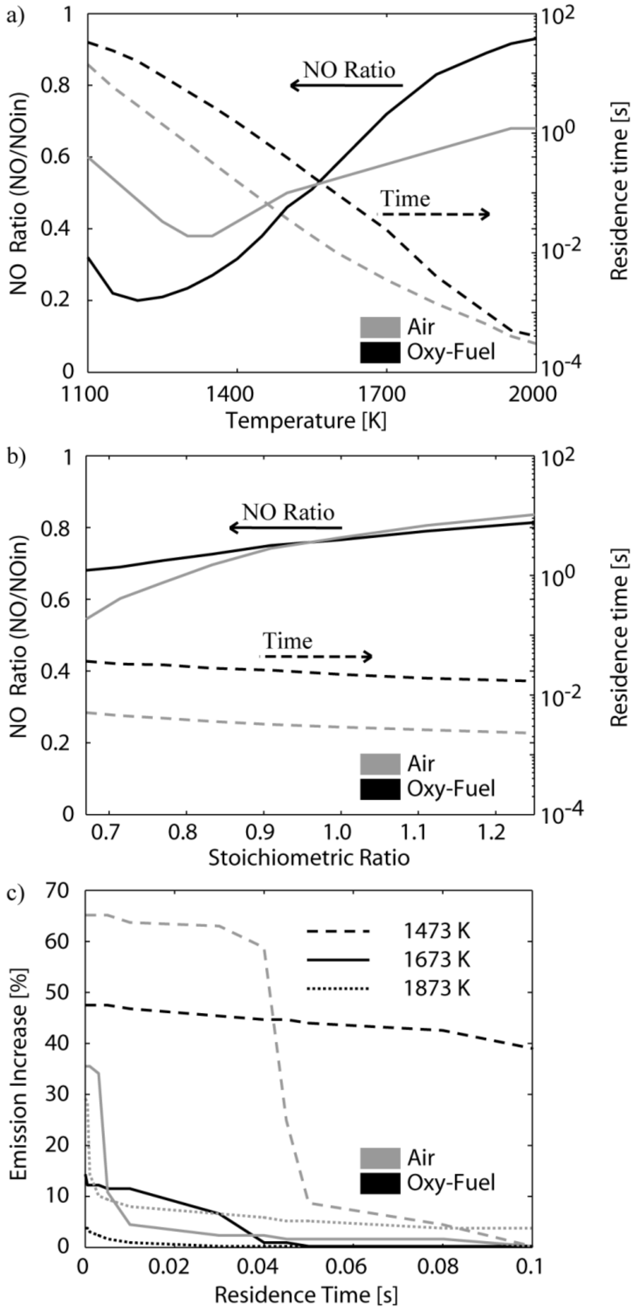

Figure 7. Influence of a) temperature (λ_{RB} = 0.7) and b) primary stoichiometric ratio (temperature = 1673K) on NO emission and the required residence time ($\tau_I´$) in Stage I. c) Increase of NO emission compared to the values at the corresponding temperatures in Fig. 7a (λ_{RB} = 0.7).

1. Temperature

The time required for the oxidation of the fuel (τ_I') and for the NO reduction both depend strongly on temperature (Fig. 7a). The reduction of NO is enhanced in the lower temperature range and reaches a minimum at around 1200K for oxy-fuel combustion. It should be noted, however, that especially at low temperatures the reduction of NO, and thereby the minimum found, is closely related to the residence time in the reburning zone, Fig. 7c.

Changes in temperature have a greater impact on reduction of NO in oxy-fuel than in air-combustion. This is due to the strong temperature dependence of CH_3 formation. The importance of CH_3 as a reducing agent to NO is enhanced under oxy-fuel conditions, and therefore the reburning process becomes more sensitive to temperature. In air-firing, NO is instead reduced to HCN by CH and CH_2 to a large extent. In general, high temperature shortens the residence time of hydrocarbon radicals, but it increases the peak concentration and reaction rate. The reduction of NO by CH_3 is more sensitive to the reduced residence time than to the other effects, and it therefore decreases with temperature. On the other hand, more CH and CH_2 are formed, which promotes the reduction of NO by these radicals whose rates increase with temperature. For air-firing, the competing influences by CH_3 and the smaller hydrocarbons reduce the impact of temperature. In Stage II, temperature has little or no influence on NO reduction in the present calculation (stoichiometric ratio of 0.7). There is no significant difference in the outlet NO concentration between Stages I and II.

Experimental work on the influence of temperature on NO_x reduction in oxy-fuel combustion is limited. The experience from air-firing is that reburning is active at temperatures around 1500K or well above 1600K[4]. The reduction of NO_x at 1500K is more sensitive to stoichiometric ratio, residence time, and gas composition in the reburning zone than above 1600K[5]. According to the results of the present work, the temperature is even more important during oxy-fuel operation than during air firing, also at high temperatures.

2. Stoichiometric Ratio

The influence of stoichiometric ratio on residence time and on NO reduction (Fig. 7b) is not as strong as that of temperature, but still significant. The relative effect on the required residence time of Stage I is similar in oxy-fuel and air combustion. However, the absolute difference in residence time between the two operation modes is large at low stoichiometric ratios. The reduction of NO in Stage I and the reformation of NO in Stage II (not shown in the figure) are both less sensitive to the stoichiometric ratio in oxy-fuel combustion than in air combustion. In Stage I, the difference in sensitivity is, as for temperature sensitivity, mainly explained by the stronger dependence of CH_3 as a reducing agent for NO in oxy-fuel combustion. A higher stoichiometric ratio increases the peak concentration of the small hydrocarbon radicals predominantly but lowers the residence time. The change in residence time is of greater importance than the slight increase in peak concentration for the reduction by the small hydrocarbons (compared to CH_3). The reduction of NO to HCN in oxy-fuel combustion is, thereby, less influenced by high stoichiometric ratios because of greater dependence on CH_3 as a reducing agent than during air combustion. For similar reasons the route of NO to HCNO is less affected during oxy-fuel operation. In Stage II, the concentrations of O, OH and O_2 are especially important for the oxidation of the intermediate species to NO. In oxy-fuel combustion, the increase in radicals resulting from higher stoichiometric ratio is moderated by the elevated CO_2 concentration. Therefore, the formation of NO from HCN during oxy-fuel combustion is less sensitive to increased stoichiometric ratio than in air combustion.

The influence of stoichiometric ratio has been investigated previously in both modeling and experimental studies[8-9, 11-14], with a consensus that the NO_x reduction decreases when the stoichiometric ratio increases, but also that the reduction is less sensitive to an increased stoichiometric ratio in oxy-fuel combustion than in air-combustion. This work shows that oxy-fuel conditions change the combustion chemistry in three ways, important to the influence of stoichiometry: the residence time in the reducing zone is affected, the dominant routes for reduction differ, and the conditions for oxidation of intermediate species change.

3. Residence Time

Figure 7c shows the increase in the emission from Fig. 7a (at three temperatures) as a function of time before secondary oxygen injection (τ_{II}). As discussed above there are two important differences between the combustion chemistry in air and oxy-firing, which influence the sensitivity to residence time: 1) the required residence time for oxidation of fuel and nitrogen intermediates is longer in oxy-fuel combustion than in air combustion, the requirement is increased at lower temperature or lower stoichiometric ratio; 2) the sensitivity of NO reduction to an increase in stoichiometric ratio, and thereby to secondary oxygen injection, is lower in oxy-fuel combustion. The two effects counteract one another in terms of NO reduction. At 1473 and 1673 K, oxy-fuel combustion is more sensitive to residence time than air-firing in the sense that the reduction of NO starts to decay already at relatively long residence times (e.g. at 1473 K and 0.1 second residence time the rise of emission is 40% from the ideal case for oxy-fuel and 0% for air). However, this effect is never as large as observed at short residence times in air-firing (the maximum increase for air is approaching 70%). The difference between air- and oxy-firing with respect to required residence time is stronger at lower temperature. This results in a higher sensitivity to residence time in oxy-fuel combustion at low temperatures (1473K), although the maximum increase remains higher for air-firing. At high temperatures (1873K) the NO reduction is fast and the sensitivity to residence time is low for both air and oxy-fuel combustion.

4. Oxygen Concentration

In a practical case, the oxygen concentration in the oxidizer is strongly connected to the flame temperature. Due to the higher heat capacity of CO_2 compared to N_2, oxy-fuel combustion requires higher oxygen concentration in the feed gas than air-firing (~30 compared to 21 volume %) to match the temperature profile of an air-fired flame. The excess oxygen in the furnace is in the same range for air and oxy-fuel conditions and the oxygen concentration in the flame, which is discussed in this section, converges. However, it is possible that the reburning zone will experience an increased oxygen concentration (O_2-CO_2 ratio) in oxy-fuel combustion compared to air-firing due to the lower reaction rate and higher inlet oxygen concentration. Oxygen concentration is critical to combustion chemistry. Higher concentration increases the amount of chain-carrying radicals and shortens the time required for hydrocarbon oxidation (Stage I). In this section, the O_2-CO_2 ratio at the inlet of the investigated flame zone in the oxy-fuel case is increased in two steps (from 0.004 to 0.02 and 0.06) to match the residence time of Stage I and the peak concentration of the hydrogen radical in oxy-firing with those of air-firing. These two levels represent a drastic increase in oxygen concentration, but are chosen because the discussion above concluded that residence time and concentration of the H-radicals are important differences between air and oxy-firing.

Figure 8 shows concentration profiles of NO, HCN, CH_3, and the sum of CH_2 and CH in the reburn zone (Stages I and II) for matching residence times (Fig. 8a) and matching concentrations of the hydrogen radical

(Fig. 8b) in oxy-fuel combustion and in air-firing as a reference. Generally, the increase in oxygen concentration enhances NO emission. The reduction of NO in Stage I is similar in all cases presented. However, when the oxygen concentration increases, more NO is formed in Stage II. When the residence times are similar (Fig. 8a), the difference in the role of CH_3 and CH_{1-2} between air and oxy-fuel becomes obvious; the concentration of CH_{1-2} is higher during air-firing, although the total concentration of hydrocarbons is higher in oxy-fuel combustion.

The reaction routes of oxy-fuel combustion approach those of air-firing when the oxygen concentration increases. In Stage I more NO is reduced directly to HCN (Fig. 6), and other reactions such as HCNO to NCO and the formation of HNCO and NH_2 from NCO become more important. However, increased oxygen concentration is more critical to NO formation in Stage II than to the reduction in Stage I. Also here the conventional routes of nitrogen chemistry (i.e.through the amine-pool) become more active with increasing oxygen concentration. This is achieved through enhanced formation of NH from NCO and NH_2. NH_2 is mainly formed via the route from HCN through HNC and HNCO to NH_2. The peak concentration of chain-carrying radicals and the reaction activity increases with oxygen concentration. Then, the relative order between the radicals becomes more important and the oxidation of the nitrogen fed to the amine-pool to NO is enhanced due to the switch from H- to OH-radicals in oxy-fuel combustion.

It has been shown previously[13] that, besides the combustion temperature, the inlet concentration of oxygen to the furnace has limited influence on NO_x reburning reduction. If this finding is related to the results of the present study, the small influence of inlet oxygen concentration on NO reduction can be interpreted as the oxygen concentration in the reburn zone is independent of the inlet oxygen concentration. The oxygen concentration in the oxidizer is often chosen to achieve flame temperatures similar to air-firing. In this investigation (where the temperature is constant in the various cases), it is shown that an increased oxygen concentration in oxy-fuel combustion compared to that in air conditions, besides similar temperature profiles, also makes the nitrogen chemistry more similar to the air-fired case, although important differences remain.

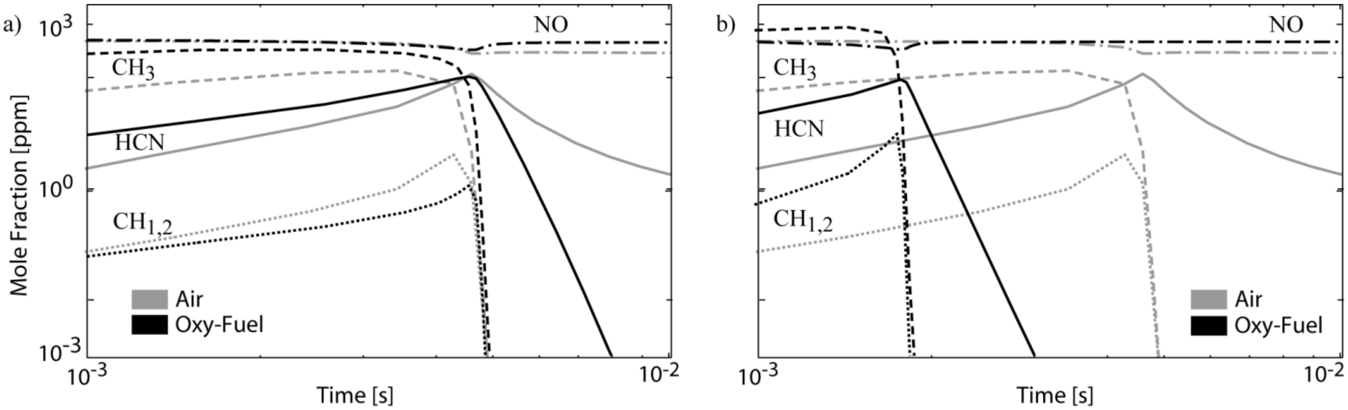

Figure 8. Concentration profiles of NO, HCN, CH_3 and $CH_{1,2}$ in oxy-firing with a) the same τ_I (O_2-CO_2 ratio 0.02) and b) the same peak concentrations of the H radical (O_2-CO_2 ratio 0.06) in air and oxy-firing. Temperature = 1673K and λ_{RB} = 0.7.

5. Recirculation Ratio

Besides the chemical effects discussed, the emission of NO_x (NO_{em}) depends on the fraction of flue gas or NO_x which is recycled back to the flame (θ = recycle ratio). The NO_x reduction ($X_{red} = 1-NO/NO_{in}$) in oxy-fuel combustion becomes less efficient and decreases by around 50% when λ_{RB} increases from 0.7 to 1.2 (Fig. 7b) due to chemical effects. However, when λ_{RB} increases, more NO_x is recycled back to the flame; consequently more NO_x is reduced. A rise in λ_{RB} from 0.7 to 1.2, with around 70% more flue-gas recycle will therefore only have a small influence on NO_x emission (~10% decrease in the investigated interval) according to,

$$\mathrm{NO_{em}} \propto \frac{(1-\theta)}{(1-\theta)+\theta \mathrm{X_{red}}} \tag{4}$$

Furthermore, the oxygen concentration of the oxidizer (C_{O2}) affects the amount of NO_x recycled to the furnace (θ),

$$\theta \propto \frac{1-C_{O2}}{C_{O2}} \tag{5}$$

According to Eqs (4) and (5), smaller θ, or higher oxygen concentration, leads to higher NO_x emission besides the chemical effects.

Conclusions

This work is a theoretical investigation of reburning reactions under oxy-fuel conditions simulated in a plug-flow reactor. Differences in combustion chemistry, performance of NO_x reduction by reburning and its sensitivity to combustion parameters in air and oxy-fuel combustion are investigated by means of a detailed reaction mechanism. It is concluded that the changed composition of the radical pool with reduced concentration of the H-radical when N_2 is substituted with CO_2 influences reburning reduction both directly and by the altered formation and oxidation of hydrocarbon radicals. Oxy-fuel combustion makes reburning reduction more sensitive to combustion temperature but less sensitive to stoichiometric ratio. Altered oxidation of hydrocarbon radicals under oxy-fuel conditions and a stronger dependence on CH_3 relative to CH_{1-2} as a reducing agent are the major explanation for the changed sensitivity to combustion parameters. Furthermore, the amount of recycled flue gas and the oxygen concentration in the reburning zone are of great importance to combustion and nitrogen chemistry, as well as to the achieved reduction of NO_x. Increased oxygen concentration in oxy-fuel combustion makes the nitrogen chemistry more similar to air-firing, besides effects on the temperature profile. These are the important differences to consider when optimizing oxy-fuel combustion to limit the emission of NO_x.

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