

Effect of HCl on NO Formation during CO/NH₃ Combustion in an Entrained Flow Reactor at 1023–1223 K

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ABSTRACT: Biomass and coal that contain high amounts of chlorine release HCl during combustion. There is no universal agreement regarding the effect of HCl on NO formation. To investigate the effect of HCl on NO formation, CO/NH₃ combustion experiments and simulations were conducted in an entrained flow combustion reactor at 1023–1223 K. The experimental results show that the HCl addition tends to inhibit NO formation at low temperatures and exhibits promotion effects when the temperature is increasing and a temperature enhancement tends to inhibit NO formation. The simulation results provide evidence that the HCl addition inhibits NO formation by reducing the concentrations of the H, O, and OH radicals.

1. INTRODUCTION

Halogens (F, Cl, Br, etc.) often exist in solid fuels, such as coal, biomass, municipal solid waste (MSW), etc., and, in particular, the content of chlorine or bromine is over 1% in some types of coal and biomass.¹ Halogens in fuels influence combustion,^{2–5} and chlorine is generally released as HCl and Cl₂. HCl and Cl₂ are well-known to act as inhibitors by catalyzing the recombination of radicals to decrease the amount of O, H, OH, and HO₂ radicals in the flames.^{6–13} Glarborg¹⁴ reviewed that the pollutant formation and emissions will be influenced by hidden interactions (S, Cl, etc.). Some researchers have reported that the addition of HCl or other halides leads to an increase in CO emission^{9–13} in fluidized bed combustors during the combustion of gaseous fuel or coal, which is because halogen addition suppresses the concentrations of radicals (O, OH, etc.). Hence, the oxidation of CO to CO₂ is significantly inhibited.

The addition of halogens not only suppresses CO oxidation but also affects the chemical reactions of nitrogen during combustion. To date, there is no universal agreement regarding the effect of halogens on NO formation during combustion. A lot of work had been conducted to study the effect of HCl on pollution emissions in fluidized bed combustors at a relatively lower temperature. Julien et al.,¹² Winter et al.,^{15,16} and Gokulakrishnan and Lawrence^{17,18} reported that the formation of NO_x decreased as a result of the addition of halogens in circulating fluidized bed combustion (CFBC) or fluidized bed combustion (FBC). However, Liang et al.¹⁰ and Anthony et al.^{11,13} confirmed that halogens enhanced the formation of NO_x in FBC. Bloomer and Miller¹⁹ reported that NO_x increased when methyl chloride/propane chlorine mixtures were combusted in FBC. Winter et al.²⁰ and Lu et al.²¹ found that iodine addition increased NO_x emission in CFBC or FBC.

Furthermore, a few researchers also found the influence of halogens on combustion at a higher temperature in some other burners. Mao et al.²² found that the NO emission level from the air-staged combustion of methyl amine (CH₃NH₂) decreased

when methyl chloride (CH₃Cl) was added. Wei et al.²³ measured NO_x profiles along the reactor length with HCl addition during pulverized coal flame. The results clearly show that NO_x formation reduces with an increasing HCl concentration. However, Linak et al.²⁴ reported that the formation of NO is not significantly reduced by chlorine in a swirling burner. Molina et al.²⁵ reported that HBr addition altered NO production depending upon the temperature during char combustion; the presence of HBr decreased NO production by 80% at 1170 K, whereas HBr addition decreased NO production by 20% at 1570 K.

The NO formation induced by the HCl addition is determined by the fuel type and combustion conditions. The concentrations of HCl and NO_x precursors (NH₃) are determined by the fuel types, whereas the field of laminar or turbulence flow, the temperature, and the concentration of the species (e.g., CO, O₂, NH₃, NO, etc.) are determined by combustion conditions (such as gas combustion, pulverized fuel combustion, FBC, CFBC, etc.). In addition to homogeneous reactions, the effect of HCl on NO formation can arise from the catalysis of ash or bed materials. To simplify the combustion conditions, experiments were conducted to investigate the effect of the HCl addition on NO formation in an entrained flow combustion reactor (EFCR), where the combustion conditions are well-controlled by adjusting the species concentrations and temperatures.

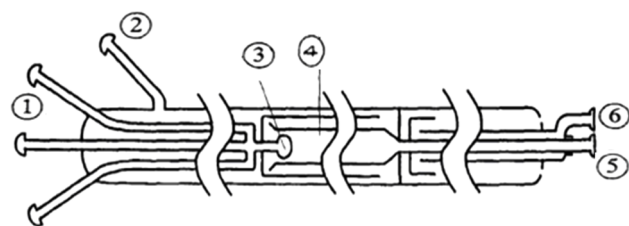
2. EXPERIMENTAL SECTION

An EFCR was used to investigate the effect of HCl on CO and NO emissions during combustion, and the structure (see Figure 1a) was similar to that used at the Technical University of Denmark (DTU), which has been described elsewhere in detail.²⁶ The reactors were designed to operate in the plug flow mode because of the slow gas

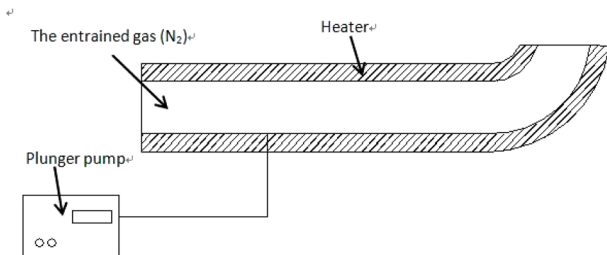
Received: December 16, 2016

Revised: January 20, 2017

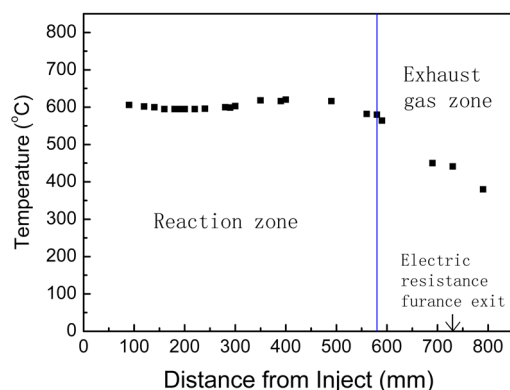
Published: February 1, 2017



(a) Entrained flow combustion reactor



(b) Acid liquid gasification device



(c) Temperature distribution of the reactor

Figure 1. (a) Entrained flow combustion reactor: (1) entrance for the reactant gas, (2) entrance for the main gas (N_2/O_2), (3) nozzles for the reactant gas jetting, (4) main reaction zone, (5) exit for the reacted gas, and (6) entrance for the cooling gas and temperature profiles of the reactor, (b) acid liquid gasification device, and (c) temperature distribution of the reactor.

velocity along the reactor. The dimensions of the reaction tubes were selected to minimize the axial dispersion in the reactors at given laminar flow conditions. A comparison of two-dimensional (2D) calculations and ideal plug flow calculations shows that the reactors operate close to an ideal plug flow. In the experiments, CO and NH_3 were employed as the fuels and hydrochloric acid was injected into the system as the halogen using an acid liquid gasification device (see Figure 1b). The temperature profile of the reactor is shown in Figure 1c. NH_3 is chosen as a precursor for NO_x formation, because it is the main gaseous nitrogen-containing component released from coal or char. The main gas (N_2/O_2) flowed through a quartz tube (diameter of 14 mm) and carried HCl and water vapor. The liquid HCl solution was added to the acid liquid gasification device (see Figure 1c) via a needle; thus, HCl and vapor could be obtained from it. The concentration of H_2O could be maintained at 1%, whereas HCl needed to be adjusted via the flux of hydrochloric acid solution and velocity through the acid liquid gasification device. The flux of acid liquid was controlled by a plunger pump. The acid liquid could be

gasified completely by controlling the velocity; thus, HCl existed in the gas phase. The mole ratio of $\text{HCl}/\text{H}_2\text{O}$ in the gas phase was equal to that in the liquid phase when the system stabilized. The reactants (CO and NH_3) flowed through an internal tube (diameter of 4 mm). Heat losses were minimized with an electric resistance heater that maintained the reactor tube at a stable reaction temperature. At the entrance of the reaction section, the spherical end of the internal tube had four small drilled orifices. Through the orifices, the reactants flowed out vertically with the tube axis and were quickly mixed with the main gas flow. The length of the reaction zone was 600 mm, and the diameter was 14 mm. In the experiments using the $\text{CO}/\text{NH}_3/\text{O}_2/\text{H}_2\text{O}/\text{N}_2/\text{HCl}$ system, water and dense hydrochloric acid were mixed with dilute acid as needed.

The concentrations of gaseous N_2 , O_2 , CO, and NH_3 were controlled separately by mass flow controllers with a 1% error, and the solution content was controlled via a water injector pump with a 3% error. In the tests, the solution was vaporized steadily using a preheater, and then the gas mixture flowed into the reactor. The initial total gas flow rate was kept at 4 L/min at 293 K and 0.1 MPa. In the CO/NH_3 combustion system, the mixture of gases consisted of 3% O_2 , 3% CO, and 1% H_2O , and NH_3 and HCl were adjusted as required. N_2 was used as the gas balance. The gases were deacidified by sodium hydroxide solution and then dehydrated by silica gel, and they were then removed and placed in gas analyzers. NO was determined using online chemiluminescent NO_x analysis (model NOA-305, Shimadzu, Japan) with an uncertainty of 1%. O_2 and CO were measured continuously using a portable gas analyzer (model 3500, Landcom), and their errors were 1 and 4%, respectively.

The chemical kinetic behavior of the reactants was modeled via the Sandia SENKIN program for CHEMKIN subroutines.^{27,28} The program solves the conservation equations for mass and energy, and it can calculate the temporal evolution of mole fractions of species for a homogeneous mixture in a closed reactor. Simple hydrocarbons ($\text{C}_1\text{--}\text{C}_4$) were documented in ref 29, and the chlorine reactions were selected from refs 30–32 and incorporated into the mechanism. The mechanism included 1112 reversible reactions and 181 species. In the simulation of adding HCl for NO reduction using the Sandia SENKIN model, an adiabatic system at a constant temperature ($T = 1023$ K) and solving the energy equation was used to model the NO reduction process, and the residence time of the gas reactions was 0.25 s.

3. EXPERIMENTAL AND SIMULATION RESULTS

3.1. Experimental Results. **3.1.1. Effect of HCl on CO Emission.** In Figure 2, the CO emission is shown during combustion with additions of various concentrations of NH_3 and HCl. The experimental results indicate that CO emission increases with the HCl addition. HCl inhibits CO oxidation via the following three reactions:

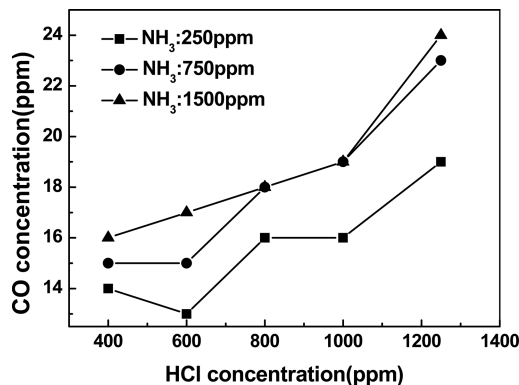


Figure 2. Concentrations of CO emission from combustion at 1173 K, 0.1 MPa, 3% O_2 , 3% CO, 1% H_2O , and using N_2 as the gas balance.

As a result of the consumption of the H radical, the formation of the OH radical is limited by the following reaction:



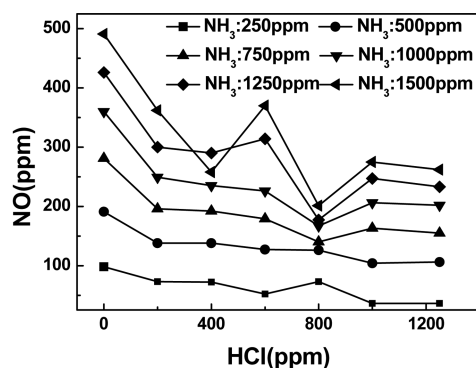
Thus, HCl inhibits the oxidation of CO via the following reaction:



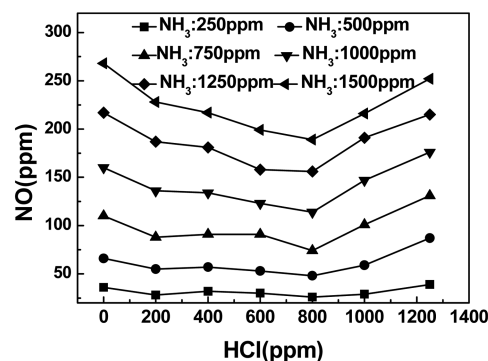
This obviously increases the CO emission and agrees with the experimental results. Additionally, as shown in Figure 2, the CO emission increases with increasing amounts of NH_3 when the initial CO concentration is kept constant. A small amount of NH_3 may also inhibit the CO oxidation. Similar results at different temperatures are shown in a previous paper.³³

3.1.2. Effect of HCl on NO Emission. The NO emission as a function of the NH_3 and HCl concentrations in gas combustion is shown in Figure 3. NO formation was determined by the synergistic effect of the HCl concentration and temperature. At 1023 K, the existence of HCl mainly inhibits the NO formation and decreases the NO emission (Figure 3a). For example, at an initial 750 ppm of NH_3 , the final emission of NO decreases from 280 to 155 ppm when HCl is increased from 0 to 1250 ppm. The total reduction ratio of NO reached 40%. As the reaction temperature increased, the effect of the HCl addition on the NO formation changed gradually. At 1173 K (Figure 3b), the NO formation reduces when the HCl concentration increases from 0 to approximately 800 ppm. Under this condition, NO formation is apparently inhibited by the HCl addition. As the added HCl concentration increases to more than 800 ppm, the NO emission begins increasing in a stable manner. Here, the HCl addition enhances NO formation. At 1223 K (Figure 3c), the NO formation was affected very slightly by the small amount of HCl that was added; thus, NO emission is relatively stable when the HCl concentration increases from 0 to 400 ppm. When the HCl concentration is over 800 ppm, the NO emission begins to obviously increase, which means that, under this condition, the existence of a large amount of HCl might enhance the transformation from NH_3 to NO. The results in Figure 4 indicate that the reaction temperature and HCl concentration play an important role in the effect of HCl on NO formation.

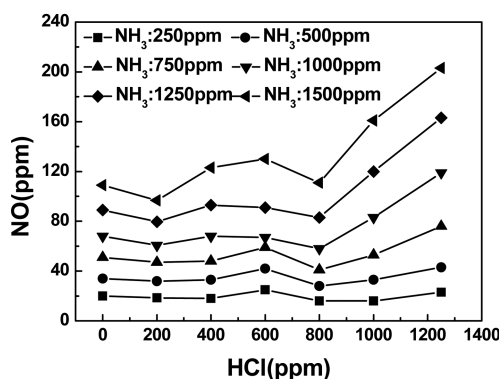
3.1.3. Effect of the Temperature on NO Emission as a Function of the HCl Addition. In Figure 4a, when CO/ NH_3 combusts at 0 or 1250 ppm of the HCl addition, the NO concentration decreases as the temperature increases from 1023 to 1223 K; however, with 600 ppm of HCl addition, the NO concentration rises slightly when the temperature first increases from 1023 to 1073 K and then decreases abruptly. The effect of HCl on the NO emission is more obvious at lower temperatures (1023–1173 K) than at high temperatures (1173–1223 K). Increasing the temperature suppresses the inhibition of HCl on NO formation. At higher temperatures (>1173 K), HCl even enhances the formation of NO. Without the HCl addition, the NO concentration decreases from above 270 to below 50 ppm as the temperature increases, whereas the NO concentration is reduced by 80 ppm after 1250 ppm of the HCl addition. These results indicate that the HCl addition suppresses the effect of the temperature on NO formation. Figure 4b shows the results for NO formation at 1500 ppm of initial NH_3 . Except for the curve of 600 ppm for the HCl addition, the results are very similar to that of Figure 4a, which indicates that the NO concentration decreases continuously as



(a) 1,023 K



(b) 1,173 K



(c) 1,223 K

Figure 3. Concentrations of NO emission from combustion at 0.1 MPa, 3% O_2 , 3% CO, 1% H_2O , and using N_2 as the gas balance.

the temperature rises. The experimental temperature rose from 1023 to 1223 K, which is within the temperature range of the DeNO_x reaction upon the addition of NH_3 . The peak temperature of kinetics of DeNO_x reactions is near 1100 K. The major reactions³⁴ can be expressed as



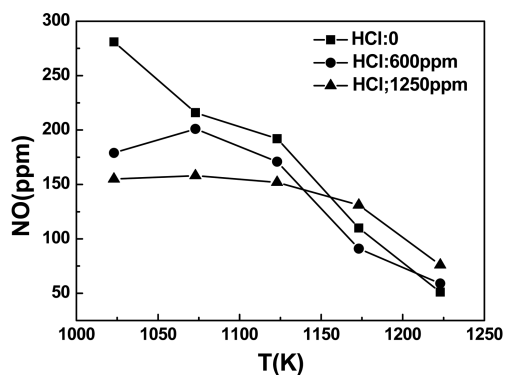
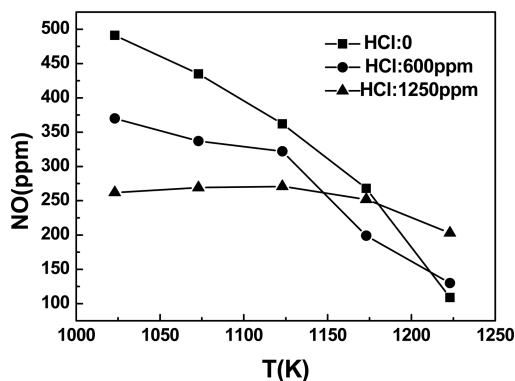
(a) NH_3 : 750 ppm(b) NH_3 : 1,500 ppm

Figure 4. Effect of the temperature on the NO formation as a function of the addition of NH_3 and HCl.



When the experimental temperature is near 1100 K, eqs R7 and R8 become dominant as the temperature is increased; therefore, the NO concentration is reduced, suggesting that NO formation is inhibited. The same results were obtained from the experiments (see Figure 4), except for the curve for 600 ppm of HCl and 750 ppm of NH_3 addition.

3.1.4. Effect of the CO Concentration on NO Formation with the HCl Addition. To study the equivalence ratio on NO formation, the CO concentration was varied from 3 to 6.5% and the O_2 concentration was held constant at 3%, corresponding to oxygen-rich or -lean conditions. Figure 5 indicates that the CO concentration affects NO formation. More NO was formed under oxygen-lean conditions than under oxygen-rich conditions. Although the oxygen was lean for combustion when CO was held at 6.5%, NH_3 still tended to form NO. These results are consistent with the studies reported by Suhimann and Rotzoll.³⁵ In their experiments, adding CO to the $\text{NH}_3/\text{NO}/\text{O}_2$ system led to more NO release. This indicates that sufficient CO combustion might enhance the oxidation of NH_3 to NO because it can supply more radical sources.

3.2. Simulation Results. 3.2.1. Reaction Path Analysis of the Effect of HCl on NO Formation. To investigate the NO formation mechanisms, a reaction pathway flux analysis was performed using MixMaster (a Python program that is part of

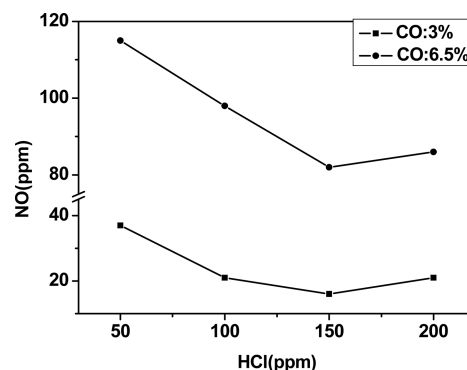
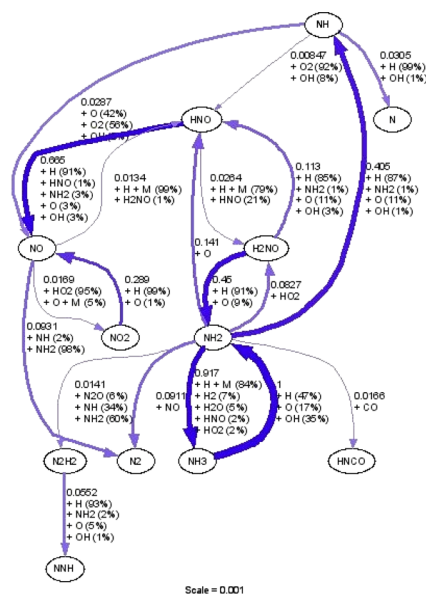
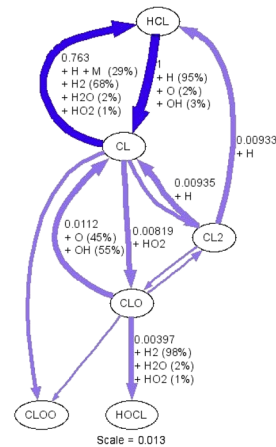


Figure 5. Effect of the equivalence ratio of CO/O_2 on NO formation at 1223 K, 0.1 MPa, 3% O_2 , 1% H_2O , 500 ppm of NH_3 , and using N_2 as the gas balance.

the Cantera suite) and the integral path analysis was based on a conserved scalar approach to the reaction fluxes.³⁶ Figure 6a



(a) The path of NO formation



(b) The path of the HCl-consuming radicals, H, O and OH

Figure 6. Reaction path analysis of the effect of HCl on NO formation at 1023 K, 0.1 s, and 800 ppm of HCl.

illustrates the detailed reaction pathway diagram for N-containing species at 1023 K for 0.1 s and 800 ppm of HCl, where the relative width of the arrows indicates the pathway importance. The most important reaction path is “1”. The importance of the other reaction paths is in comparison to “1”, and the smaller number shows that the reaction is unimportant. Figure 6a indicates that NO is formed via the oxidation of NH and HNO. The detailed pathways of NO formation are provided below.

(1) Detailed pathway of NO formation via NH:



(2) Detailed pathway of NO formation via HNO:



The reaction pathway diagram also indicates that NO would be reduced by the following reaction pathways:



From the above analysis, the reaction pathways of N-containing species are complicated. The NH_2 , NH , and HNO free radicals derive from NH_3 , where H , O , and OH are intermediates at different stages. These free radicals can not only produce NO via eqs R9–R18 but also reduce NO via eqs R19 and R20. The net effect of NH and HNO is NO formation, and the net effect of NH_2 and NH is NO reduction. This conclusion is also similar for the DeNO_x reaction. The high concentrations of H , O , and OH can promote NH_2 , NH , and HNO formation, which easily increase the NO formation. However, concentrations of H , O , and OH that are too high always make NH_3 convert largely into NH_2 and NH to easily reduce NO into N_2 . Thus, appropriate concentrations of H , O , and OH are important for controlling NO formation.

To further investigate the effects of the chemical mechanisms of HCl on NO formation, Figure 6b illustrates the detailed reaction pathway diagram for Cl-containing species at 1023 K for 0.1 s and 800 ppm of HCl. Adding HCl can effectively consume the H radical, leading to a reduction of O and OH radicals. This will inhibit NO formation via the following reactions:



Wei et al.³³ also found two main elementary reactions to promote NO formation.



The effect of inhibition is stronger than that of promotion in the similar conditions of this study. Therefore, the HCl addition can inhibit NH_3 oxidation by consuming H , O , and OH radicals, thus reducing NO formation.

3.2.2. Simulation Results of the Effect of the HCl Concentration on NO Formation. To further explore the effect of HCl on NO formation, the simulation results for various HCl concentrations were analyzed. Here, the concentrations of O_2 and CO were kept constant at 3%, H_2O was kept constant at 1%, and NH_3 was kept constant at 0.075%, whereas the HCl concentration was changed from 0 to 0.12% and N_2 was used as the gas balance. Figure 7 indicates that the

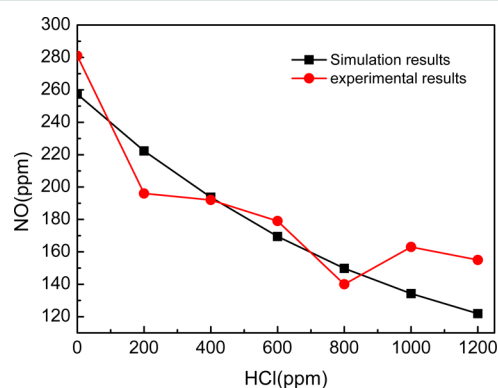


Figure 7. Effect of the HCl concentration on NO formation at 1023 K, 0.1 MPa, 3% O_2 , 3% CO , 1% H_2O , 0.075% NH_3 , and using N_2 as the gas balance.

HCl addition can inhibit NO formation, and the amount of NO gradually decreases with an increase of the HCl concentration. When the HCl concentration reaches 800 ppm, the NO concentration varies slightly with the HCl addition. These results are similar to the experimental results. As shown in Figure 8, adding 800 ppm of HCl results in a decrease in H radicals from 230 to 75 ppm, a decrease in O radicals from 400 to 190 ppm, and a decrease in OH from 160 to 110 ppm. The concentration of H radicals without HCl is 3 times more than that with 800 ppm of HCl, and the concentration of O radicals is less than half of that without HCl. Figure 8 also indicates that adding HCl can inhibit NO formation by inhibiting the concentrations of O, H, and OH radicals.

3.3. Discussion. The detailed mechanism of the $\text{CO}/\text{NO}/\text{HCl}$ system was also used to analyze the experimental results of the CO/NH_3 co-combustion upon the HCl addition. Calculations were performed for a mixture with an initial 3% CO , 3% O_2 , 1% H_2O , 750 ppm of NH_3 , 0 or 800 ppm of HCl, and a balance of N_2 at 0.1 MPa in the reactor at 1023 K. As shown in Figure 3, the experimental results indicate that adding HCl inhibits NO formation before 800 ppm of HCl were added. The experimental results at 1023 K and with 750 ppm of NH_3 are very similar to the simulation results shown in Figure 7. However, with the above conditions, including 800 ppm of HCl (panels a–c of Figure 3), HCl might promote NO formation. However, this may not be explained by the present reaction mechanisms.

The effect of HCl on the concentrations of radicals with time is shown in Figure 8. In Figure 8a, without the HCl addition, the concentrations of the O, H, and OH radicals reach peak values at approximately 0.04 s. As shown in Figure 8b, with the

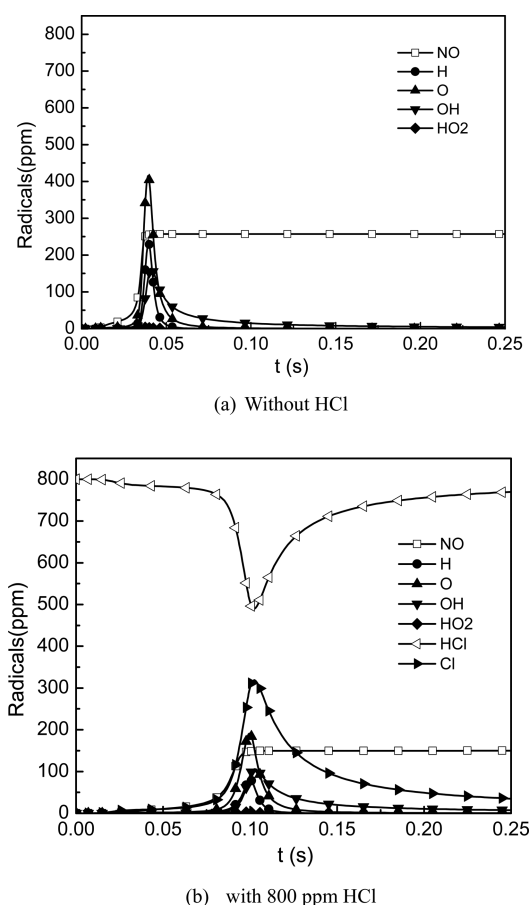


Figure 8. Effect of HCl on the O, H, and OH radical concentrations.

HCl addition, the peak time for O, H, and OH radicals was delayed to 0.1 s. This indicates that HCl not only suppresses the peaks of the O, H, and OH radicals but also delays the ignition of CO. Therefore, both CO oxidation and NO formation are inhibited by HCl.

In solid fuel (such as coal, biomass, and waste) combustion relating to fluidized beds, CO and NH₃ are the main species included in the released volatiles. For a CO/NH₃ co-firing system, the NO formation is affected by the synergic action of the HCl concentration and temperature. When the initial gaseous concentration is kept constant, the higher temperature prefers to inhibit NH₃ oxidation to NO. In the actual combustion of solid fuel, besides the homogeneous gaseous combustion, the combustion flow field, the heterogeneous gas–solid combustion, the ash behavior, and even the surface effects of the bed material (in FBC or CFBC) may affect the final NO emission. Therefore, for combustion that occurs in different reactors and fuel types, NO emission exhibits different and even adverse variations with varying HCl concentrations.

4. CONCLUSION

The effect of HCl on NO formation in combustion of a CO/NH₃ system was investigated experimentally in an EFCR. The results show that NO formation is sensitive to the concentration of HCl and the temperature during the co-combustion of CO/NH₃. With an increasing temperature, the effect of HCl on NO formation changes from inhibition to promotion. When the initial gas concentrations are constant, a higher temperature results in the release of less NO. The

equivalence ratio of CO/O₂ also appears to affect NO formation. NO emission under oxygen-lean conditions is more than that under oxygen-rich conditions. A detailed kinetic mechanism was used to analyze the experimental results of the CO/NH₃ co-combustion when HCl was added. We determined that HCl inhibits the formation of OH and affects NO formation via the reactions of H, O, and OH with NH₃, NH₂, NH, and HNO.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the National Key Research and Development Plan of China (2016YFB0601503) is gratefully acknowledged. The authors also thank Prof. Peter Glarborg and Dr. Jingwei Zhang for their assistance.

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