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Experimental investigation and numerical simulation of CO oxidation with HCl addition

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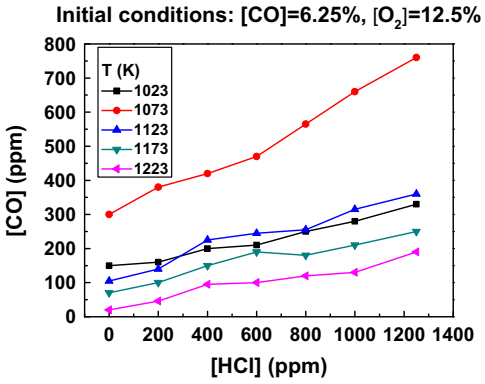
HIGHLIGHTS

- Experiment is operated under different temperatures and equivalence ratios in an EFR.
- Simulation is conducted by CFD coupled with reduced reaction mechanism.
- Inhibition of HCl on CO oxidation is affected by equivalence ratio and temperature.
- HCl inhibits CO oxidation mainly through suppressing OH production.

GRAPHICAL ABSTRACT



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ABSTRACT

Chlorine is rich in biomass and some coals and significantly released as HCl(g) during combustion process, and this promotes the recombination of free radicals OH, H, O, and HO_2 and further influences CO oxidation. In this paper, the inhibition effect of HCl on CO oxidation is investigated by experiment and numerical simulation. The experiment is operated under different reaction zone temperatures and equivalence ratios in an entrained flow reactor. And the numerical simulation is conducted by CFD software coupled with reduced reaction mechanism. The results indicate that HCl addition obviously inhibits CO oxidation under oxygen-rich condition, and the inhibition enhances as HCl concentration rises, but weakens as temperature increases. Under chemical equivalent and oxygen-lean conditions, the inhibition effect is limited.

1. Introduction

Chlorine is rich in biomass and some coals, and it is either released or retained in ash during combustion, which causes fouling, slagging, deposition or corrosion in the boiler [1–6]. Compared with coals, biomass has high content of chlorine, and significant amount of it is released as KCl(g), NaCl(g), or HCl(g), etc. [7–13,19], which promotes the recombination of free radicals OH, H, O, and HO_2 at high temperature and decreases their total amount, and results in an inhibition effect on CO oxidation [14–26].

Roesler et al. [14–16] developed a detailed kinetic model for moist CO oxidation inhibited by HCl. The model was validated against experimental data and showed good agreement. The results revealed that trace quantity of HCl could significantly

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inhibit CO oxidation. At high temperature, the chain termination reactions in the inhibitory cycles were primarily $H + Cl + M \leftrightarrow HCl + M$ and $Cl + Cl + M \leftrightarrow Cl + M$. But the principal chain terminating step at 1000 K was found to be $Cl + HO_2 \leftrightarrow HCl + O_2$. Glarborg [19] investigated how trace species affects overall combustion process, and he also established a general reaction model. It is presumed that inhibition took place through A cycles: $HCl + H \leftrightarrow H_2 + Cl$ and $HCl + OH \leftrightarrow H_2O + Cl$. As Cl concentration built up in the post-flame region, the inhibiting cycles competed with B cycles: $Cl + HO_2 \leftrightarrow ClO + OH$ and $ClO + CO \leftrightarrow Cl + CO_2$, which corresponded to overall reaction: $CO + HO_2 \leftrightarrow CO_2 + OH$. The competition between A and B cycles determined whether the chlorine had an overall promoting or inhibiting effect on CO oxidation. Wei et al. [22] investigated the influence of HCl on CO emission in combustion, the results indicated that HCl not only promoted the recombination of radicals O, H, and OH, but also accelerated the chemical equilibration of radicals. The influence of HCl on the radicals mainly occured at 800–1200 K. Wang and Chi [24] constructed a kinetic model of $CO/H_2/Cl_2$ mixture oxidation, the results illustrated CO conversion varied inversely with Cl/H mole ratio and increased with temperature. The reaction of $HCl + OH \leftrightarrow H_2O + Cl$ decreased OH concentration and led to low CO conversion, and CO oxidation was mainly through $H + O_2 \leftrightarrow HO_2$. The rising of reaction temperature resulted in higher OH concentration and larger reaction rate of $CO + OH \leftrightarrow CO_2 + H$. Pelucchi et al. [25] updated the high-temperature chlorine chemistry and re-examined the inhibition mechanisms involving HCl and Cl_2. It is found that the reactions containing HCl were the chain propagation reactions: $HCl + O \leftrightarrow Cl + OH$, $HCl + OH \leftrightarrow H_2O + Cl$ and $Cl + HO_2 \leftrightarrow ClO + OH$, together with the termination reaction: $Cl + HO_2 \leftrightarrow HCl + O_2$. Besides the investigations mentioned above, some other studies related to the influence of HX-type or halogen gas on fuel oxidation also had significant assistance to our research [27–31].

In this paper, the inhibition effect of HCl addition on CO oxidation is investigated by experimental and numerical simulation study. At present, most experiment and simulation studies of HCl on CO oxidation are focused on reactions in post-combustion, and the CO concentration is rather low (less than 1%) [14–16]. However, CO concentration can be up to 5% in the initial-combustion stage. Therefore, CO concentration of 1–6% is investigated. The experimental study is operated in an entrained flow reactor at different reaction zone temperatures and equivalence ratios. The numerical simulation is conducted by CFD software coupled with reduced reaction mechanism involving 12 species and 6 reactions.

2. Experimental system

Based on one-dimensional reaction flow model, an entrained flow reactor (EFR) system is applied to investigate the effect of HCl addition on CO combustion.

Fig. 1(a) shows the structure of EFR system, which is similar to those used in DTU (Technical University of Denmark) [32,33]. At the entrance of the reactor, a spherical end of the internal tube has four small drilled orifices. Through the orifices, the reactants can flow out vertically with the tube axis and quickly mix with the main gas flow. The main airflow of the reactants containing O_2, H_2O, HCl and N_2 is sent into the entrance of the EFR through a quartz reaction tube with a diameter of 14 mm and length of 590 mm. The second airflow with pure CO comes into the EFR through the four orifices and mixes with the main airflow. The total volumetric flow rate is 4 NL/min. The heat loss is minimized with electric resistance heater that maintains the reactor tube at the initial reaction temperature. CO concentration is measured by a Land gas analyzer.

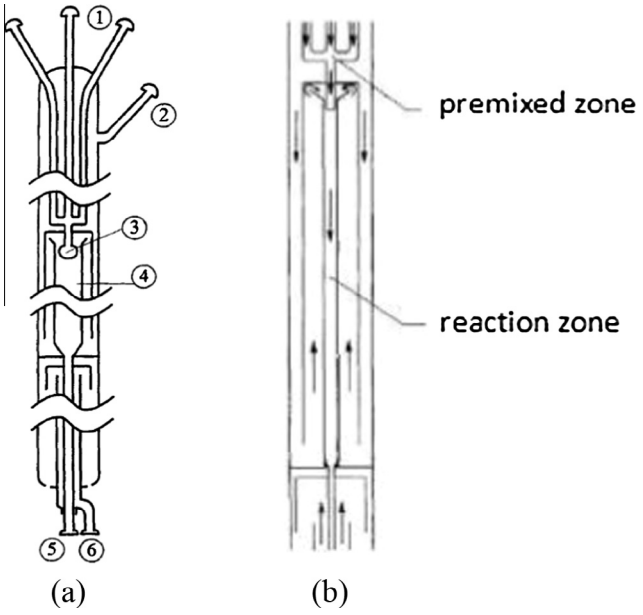

Fig. 1. Experimental system: (a) structure of EFR: ① CO inlet ② main gas inlet ③ nozzle ④ reaction tube ⑤ off-gas outlet ⑥ cooling gas inlet; (b) flow state in the EFR.

In Fig. 1(b), the front concentric tube and the nozzle together form a narrow interlayer, which corresponding to the premixed zone. CO sprays into the premixed zone through the nozzle and strongly mixes with the main airflow. Then, the mixing gas rapidly reach the wall and flow into the reaction zone to finish the combustion. The mixing process is quite violent and complex, which related to a turbulent flow. However, due to the small size of the premixed zone and the low flow rate of the mixing gas, the Reynolds number tends to be not very high.

3. Chemical reaction model

3.1. Model establishment

A self-written program for chemical mechanism reduction is developed to implement the detailed mechanism [14,16] into CFD program. As a preliminary exploration in the present work, based on the Connect and PCAF methods [34], a skeletal mechanism (see Table 1) is obtained by reducing a detailed mechanism including 19 species and 140 irreversible reactions and containing $CO/O_2/HCl/H_2O/N_2$. Then, the QSS (quasi-steady-state) assumption method is used to distinguish the QSS species, the reduced mechanism involving 12 species and 6 reactions is obtained, as shown in Table 2. The reaction rates of the reduced mechanism are given in Table 3.

3.2. Model validation

To validate the reduced mechanism, the SENKIN code in CHEMKIN is used to calculate with the detailed, skeletal and reduced mechanism respectively, and the results show high accuracy for the reduced mechanism, as shown in Fig. 2. Coupling the reduced mechanism with CFD software, the effect of trace amount of HCl on CO combustion is simulated at different HCl concentration, reaction zone temperature, and equivalence ratio.