Fuel 233 (2018) 769–777

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

Enhancement effects of $\cdot O_2^-$ and $\cdot OH$ radicals on NO_X removal in the presence of SO_2 by using an O_3/H_2O_2 AOP system with inadequate O_3 (O_3/NO molar ratio = 0.5)

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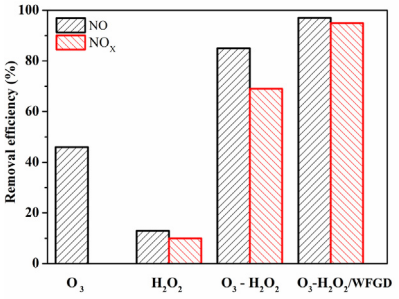
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Ozone
Advanced oxidation process
Superoxide anion radical
Nitrogen oxides
Mechanism

ABSTRACT

The O_3/H_2O_2 advanced oxidation process (AOP) was, for the first time, utilized for low-temperature NO_X removal. The present method has a high NO_X removal, which is 58% higher than the sum of that for single O_3 and H_2O_2 method with O_3/NO molar ratio of 0.5. Besides, much O_3 consumption, together with operating costs will be saved. The improved activity in O_3/H_2O_2 is due to the increased generation amount of $\cdot OH$ and $\cdot O_2^-/HO_2\cdot$ radicals than the consumption amount of O_3 when the molar ratio of O_3/NO $<$ 1, and the $\cdot O_2^-/HO_2\cdot$ radical can selectively oxidize NO into HNO_3 with a fast rate constant in a single step, while $\cdot OH$ can non-selectively oxidize NO and NO_2 also at a fast rate constant. The SO_2 in the flue gas even poses a positive effect on the NO_X removal. Absorption by NaOH solution is generally followed by the O_3/H_2O_2 method, resulting in the final 95% NO_X removal with the O_3/NO molar ratio of 0.5. Only NO_3^- ions can be detected as the liquid production through ion chromatography for the O_3/H_2O_2 method. We expect that this study can shed some lights on the route design for simultaneous NO_X and SO_2 removal.

1. Introduction

Nitrogen oxides (NO_X), as one of the major air pollutants, leads to acid rain and photochemical smog, which is harmful to the environment and human health [1]. For dealing with the terrible problem of NO_X pollution, Chinese government has issued the ultra-low emission

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https://doi.org/10.1016/j.fuel.2018.06.099
Received 28 February 2018; Received in revised form 22 April 2018; Accepted 25 June 2018

standards of NO_X (50 mg/m^3) for coal-fired power plants in 2015 [2]. The selective catalytic reduction (SCR) with NH_3 is identified as the well-known efficient route to control NO_X emission, whose temperatures of flue gas are typically from 300 to 400 °C [3]. However, it is not suitable for middle and small industry boilers because of its high cost and the imperfection of low temperature SCR application (< 150 °C) [4]. To that end, O_3 oxidation method together with Wet Flue Gas Desulfurization (WFGD) is under development to fill the gap of NO_X removal at low temperatures [5,6]. During this process, insoluble NO will be mainly converted into NO_2 at an O_3/NO molar ratio < 1.0 [7]. It was found that the NO_2 absorption efficiency was unsatisfactory in the limestone slurry [8]. As the solubility of nitrogen oxides increases with the valence state, N_2O_5 has much higher solubility than NO_2 during wet scrubbing [9]. Thus, excess O_3 may be applied for further oxidation of NO_2 to N_2O_5 to effectively improve the subsequent NO_X removal efficiency ($2NO + 3O_3 = N_2O_5 + 3O_2$). In order to promote efficient conversion of NO to N_2O_5, excessive dosage of O_3 compared with stoichiometric ratio is needed, leading to some O_3 leakage [5]. Hence, it is urgent to seek for a novel ozone-based method both to reduce the O_3 consumption and to enhance NO_X removal.

The O_3/H_2O_2 method is the most commonly used advanced oxidation process (AOP) in the water treatment field, which generates ·OH radical with strong oxidation ability to degrade the ozone-resistant compounds [10]. However, there has been few researching work related to the gas purification by the O_3/H_2O_2 AOP method. Additionally, previous articles were mainly concentrated on ·OH radical, other types of reactive oxygen radical were relatively less studied. In this study, for the first time, the O_3/H_2O_2 method was used to remove NO_X (x = 1, 2). The basic principles for the interaction between O_3 and H_2O_2 were described, and reaction mechanisms for NO_X removal were presented. Effects of different factors on NO_X removal were also investigated. The reaction products of NO_X (x = 1, 2) removal were measured and the material balance of N element was established.

2. Experimental section

2.1. Experimental apparatus

Fig. 1 shows schematic diagram of experimental setup. The removal of NO_X through O_3/H_2O_2 method was performed in a fixed-bed flow reactor at atmospheric pressure. The reactor is a quartz tube with 10 mm diameter and 220 mm length. The required H_2O_2 pH was adjusted by adding HCl (0.3 M) or NaOH (0.3 M) solutions. The reactant flue gas was prepared by mixing N_2 and small amount of concentrated NO gas (1% (v/v), balanced with N_2). O_3 was prepared by an ozone generator. Typically, the NO, O_3 and H_2O_2 were fed into the reactor, and then they were effectively mixed and reacted with each other on the sieve plate (200 mesh size). O_3 reacted with the adsorbed H_2O_2 on the sieve plate to form reactive oxygen species, which could effectively promote NO_X removal. To ensure the full reaction between O_3 and H_2O_2, the O_3 and NO were not allowed to be premixed before they arrived to the sieve plate.

The total flow of all reactant gas mixture including O_3 and simulated flue gas was 220 mL min^{-1}, and the O_3 flow was 20 mL min^{-1}. The initial gas concentrations used in the test were NO: 400 ppm, O_3 concentration: 4.8 mg·L^{-1}, O_3/NO (mol/mol): 0.5, H_2O_2 solution: 10 wt %, H_2O_2 solution pH: 6.5, H_2O_2/O_3 (mol/mol): 0.8 in different cases.

2.2. Product analysis

The concentrations of NO, NO_2, NO_X and SO_2 were detected by a flue-gas analyzer (Sensonic IR-1, European Union). Produced nitrate and nitrite ions in the solution were analyzed by ion chromatography (IC, Dionex). PL spectra of terephthalic acid (TA) solutions were obtained to measure the produced ·OH radical, by using a Labram-HR800-type spectrophotometer (Jobin Yvon Co., France) with a He-Cd laser (λ = 325 nm) as the light source. A UV–Vis spectrophotometer (T6 New Century, Beijing Persee Co., Ltd., China) was to detect the degradation of p-benzoquinone (p-BQ), which were used as a probe compound of ·OH and $\cdot O_2^-$ radical, respectively. One spectrometer (Bruker EMX-10/12) was used to record the Electron Paramagnetic Resonance (EPR) signals of ·OH and $\cdot O_2^-$ radical. The sample was prepared by injecting O_3 into a mixture of 10 mM H_2O_2 and 100 mM DMPO solution. The origin H_2O_2 and products were uniformly coated on the surface of potassium bromide, and then recorded on an IS10 spectrometer (Nicolet, Madison, Wisconsin, USA). The inlet and outlet NO, NO_X and SO_2 contents were obtained after 30 min at steady state. The removal efficiency was calculated by the following equation:

$$\eta = (C_{in} - C_{out})/C_{in} \times 100\%$$

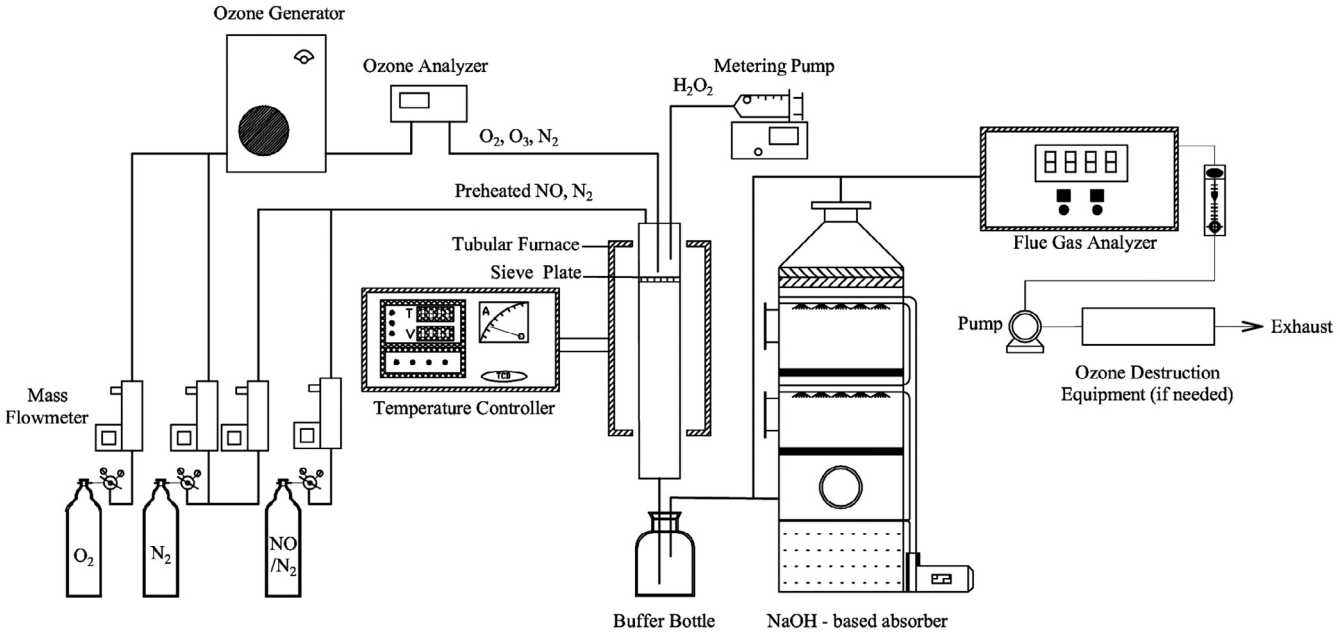

Fig. 1. Schematic diagram of experimental apparatus for denitrification by the O_3/H_2O_2 oxidation method.