Chemical Engineering Journal 232 (2013) 26–33

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Generation of reactive oxygen species in simulated flue gas under vacuum ultraviolet radiation

Junhui Ye, Jing Shang *, Han Song, Qian Li, Tong Zhu *

State Key Joint Laboratory of Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, People's Republic of China

HIGHLIGHTS

- We determine reactive oxygen species in simulated flue gas under VUV radiation.
- We examine the effects of H_2O content, O_2 content, flow rate and VUV lamp power.
- Increasing O_2 content and flow rate will increase O_3 production.
- Increasing H_2O content and flow rate will increase H_2O_2 production.
- Increasing lamp power will affect O_3 production slightly but decrease H_2O_2 production.

ARTICLE INFO

Article history:
Received 16 April 2013
Received in revised form 12 July 2013
Accepted 18 July 2013
Available online 27 July 2013

Keywords:
Flue gas treatment
VUV
Reactive oxygen species
Ozone
Hydrogen peroxide
Hydroxyl radical

ABSTRACT

Reactive oxygen species, which are responsible for the removal of SO_2 and NO_x, generated under vacuum ultraviolet (VUV) radiation in simulated flue gas ($N_2/O_2/CO_2/H_2O$ (v/v) = 74%/8%/10%/8% without SO_2 and NO_x) were determined. Under typical experimental conditions, 26.5 μmol ozone, 1.7 μmol hydrogen peroxide, and 0.3 μmol hydroxyl radical were detected. The effects of H_2O and O_2 contents, gas flow rate, and lamp power on the generation of reactive oxygen species were investigated. Results show that H_2O and O_2 contents as well as flow rate significantly affected O_3 and H_2O_2 production. High content of H_2O resulted in a decrease in O_3 production but an increase in H_2O_2 production, whereas O_2 content demonstrated the opposite effects owing to its varying absorption across sections. O_3 and H_2O_2 production increased with increasing flow rate, while their concentrations changed slightly. High-power lamps had a negligible effect on O_3 and H_2O_2 production, but O_3 production decreased and H_2O_2 production increased under extremely low-power lamp radiation. In addition, the variations of the production of reactive oxygen species were also correlated with the oxidation processes of VUV-induced simultaneous desulfurization and denitrification.

1. Introduction

Direct vacuum ultraviolet (VUV) photolysis or induced oxidation technology has been widely used as an important environmental pollution control method. The method is safe and effective. The low pressure mercury lamp with main wavelengths of 185 and 254 nm is often used as a cheap and convenient VUV source. Many organic pollutants in water have been treated using VUV photolysis, such as geosmin, 2-methylisoborneol, formic acid, 2,4-chlorophenolaceticacid, perfluorooctanoic acid, and 1,1,1-trichloroethane [1–5]. In addition to the water treatment, air pollutants such as naphthalene, H_2S, three chlorinated volatile organic compounds (chloroform, carbon tetrachloride, and trichloroethylene), benzene, toluene, and cis-1,2-dichloroethylene can also be removed [6–9]. With sufficient irradiation time, VUV can fully remove or convert pollutants to less harmful intermediates. Zhao et al. [6] demonstrated a safe and economical application of naphthalene VUV photolysis for indoor air purification. The VUV-induced pollution control mechanisms are proposed, such that pollutants can be directly decomposed by VUV light or indirectly oxidized by highly reactive species such as $^{\cdot}OH$, $^{\cdot}HO_2$, $O(^3P)$, $O(^1D)$, H_2O_2, and O_3, which are produced from VUV photolysis of small molecules, such as H_2O and O_2 [1–10]. Whether in water or gas, H_2O and O_2 can effectively absorb VUV. However, the 185 nm light penetrating depth in water is extremely short (several millimeters) because of its high concentration and absorption coefficients. The generated radicals will rapidly decay, deactivate, or react with one another without moving from the irradiated to the non-irradiated zones. This phenomenon will limit the application of VUV in large-scale water

---

* Corresponding authors.
E-mail addresses: shangjing@pku.edu.cn (J. Shang), tzhu@pku.edu.cn (T. Zhu).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.07.056

treatment plants and will incur high capital costs [11]. In contrast to the VUV photolysis of aqueous solutions, gas phase photolysis is more energy efficient [12] because the 185 nm light penetration can reach tens of centimeters in the gas phase.

The flue gas emitted by coal-fired power plants contains high H_2O and O_2 contents, which is advantageous for SO_2 and NO_x treatment using VUV. Tsuji et al. [13–15] used 172 nm Xe_2 and 146 nm Kr_2 excimer lamps as VUV sources to remove SO_2, NO, and NO_2 in N_2 or air. SO_2, NO, and NO_2 were removed by direct decomposition to S, O_2, and N_2 in N_2, whereas SO_2 and NO_2 were decomposed or chemically transformed to $–SO_4$ or N_2O_5, HNO_3, N_2, and O_2 in air. We investigated VUV-induced simultaneous desulfurization and denitrification in the presence of abundant water and oxygen. The simultaneous removal of 90% SO_2 and 96% NO_x ($NO + NO_2$) was achieved from the simulated flue gas ($N_2/O_2/CO_2/H_2O/SO_2/NO_x$ (v/v) = 73.9%/8%/10%/8%/0.08%/0.035%) under the irradiation from a low-pressure mercury lamp with main wavelengths of 185 and 254 nm. Compared with the high-energy dielectric-barrier discharge (DBD) methods, long-wavelength VUV offers the advantage of producing a high concentration of reactive species without NO_x and CO contamination in the atmosphere owing to the small absorption across sections of N_2 and CO_2 [16,17]. With the development of highly efficient VUV sources, such as microwave discharge electrodeless lamp (185 nm is equal to 12% of the total UV intensity) [7] and 172 nm Xe_2 excimer lamp (VUV emission conversion efficiency of 40%) [18], VUV exhibits greater potential in environmental pollutant treatment.

The main cause of VUV-induced simultaneous desulfurization and denitrification is the oxidization of SO_2 and NO_x by highly reactive oxygen species, such as $^{\cdot}OH$, $^{\cdot}HO_2$, $^{\cdot}O$, and O_3, which are generated from the photolysis of H_2O and O_2. The additional $^{\cdot}OH$ and $^{\cdot}HO_2$ generated through the reactions of $NO + {}^{\cdot}HO_2$ and $SO_2 + {}^{\cdot}OH/{}^{\cdot}HO_2$ improved treatment efficiency, whereas the oxidation products of NO_x, e.g., NO_2, HNO_2, HNO_3, and HNO_4, consumed massive reactive oxygen species (such as $^{\cdot}O$, $^{\cdot}OH$, and $^{\cdot}HO_2$), thereby reducing the removal efficiencies. The effects of experimental parameters such as water content (2–12%), oxygen content (2–12%), carbon dioxide content (2–18%), initial SO_2 concentration (400–1750 ppm), initial NO_x concentration (100–650 ppm), flue gas temperature (50–80 °C), flow rate (200–1000 sccm), and lamp power (4–30 W) were investigated. The result indicated that water content, oxygen content, initial NO_x concentration, flow rate, and lamp power significantly affected the simultaneous removal efficiencies of desulfurization and denitrification. High water and oxygen contents, low initial NO_x concentration, low flow rate, and high lamp power would benefit the treatment. To understand the SO_2 and NO_x VUV photolysis-induced oxidation process better, we conducted experiments to capture reactive oxygen species under various settings of the main influence factors, excluding initial SO_2 and NO_x concentrations to avoid consumption of the generated reactive oxygen species. $^{\cdot}OH$, O_3, and H_2O_2 were selected, and their variations and possible causes were discussed. The relations of $^{\cdot}OH$, O_3, and H_2O_2 with simultaneous desulfurization and denitrification were also investigated. Given that OH radical concentration is extremely low and near the detection limit, we only show its approximate production under typical experimental conditions.

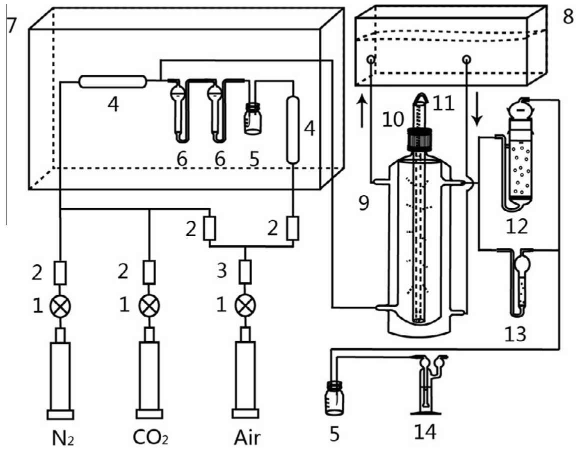

Fig. 1. Schematic diagram of the experimental system. (1) Pressure regulator; (2) mass flow controller; (3) air dryer; (4) Heating Glass Tube; (5) surge flask; (6) humidifier; (7) drying oven; (8) thermostatic water bath; (9) photoreactor; (10) quartz tube; (11) VUV lamp; (12) 600 mL U-shaped fritted purge and trap sparger; (13) 100 mL U-shaped fritted purge and trap sparger; and (14) tail gas absorber.

2. Material and methods

2.1. Experimental setup and procedure

The simulated flue gas (without SO_2 and NO_x) was composed of $N_2/O_2/CO_2/H_2O$ (v/v) = 74%/8%/10%/8%. The gas flow rate was 500 sccm. The gas temperature was 60 °C. The VUV source was an 18 W low-pressure mercury lamp. The above experimental conditions were also regarded as typical experimental conditions. Fig. 1 shows a schematic diagram of the experimental system. All experiments were conducted at ambient pressure. Compressed gas cylinders were used to provide all gases, except water vapor. Saturated water vapor was provided by two humidifiers (6), with the water in the humidifiers preheated to 60 °C. Dry air passed through the humidifiers at a constant flow rate and produced saturated water vapor mixed with dry gas, which was used to adjust the water content. The gases from the cylinders first passed through a pre-heating drying oven (7), which was thermostatically set to 60 °C, and were then heated using two heating glass tubes (4). The gases then flowed into a 2 L double-layer cylinder glass photoreactor (inner diameter 80 mm, outer diameter 115 mm, height 370 mm) (9). Water at a temperature of 60 °C was pumped from a thermostatic water bath (8) to the outer layer of the photoreactor to maintain the temperature. A quartz tube (10) was inserted into the top of the reactor and sealed with a custom-made Teflon cap, enabling the placement of the UV lamp in the tube for the even irradiation of the reactor. The simulated flue gas was balanced in the photoreactor and gas lines for 30 min. After 30 min, the UV lamp was switched on, and the simulated flue gas was irradiated by an 18 W low-pressure mercury lamp (ZW18D15Y-Z356, Cnlight, China) (11) with main wavelengths of 185 and 254 nm (185 and 254 nm are equal to 5% and 95% of the total UV intensity, respectively) [19]. The temperature of the gas line between the oven and reactor was maintained by the water flow from the water bath to prevent water condensation.

Two types of U-shaped fritted purge and trap spargers were used to trap reactive oxygen species. Ozone was trapped by a 600 mL U-shaped fritted purge and trap sparger (12), whereas the hydrogen peroxide and hydroxyl radical were trapped by a 100 mL variant (13).

2.2. Analytical methods

2.2.1. Ozone

Indigo disulfonate spectrophotometry (IDS) was used to measure the production of ozone [20]. Ozone reacts with indigo disulfonate in a 1:1 M ratio. A 500 mL extract from approximately 25 mg/L indigo disulfonate solution prepared using 0.050 mol/L $KH_2PO_4–Na_2HPO_4$ phosphate buffer solution was used to capture O_3. A 3.5 mL capture solution was obtained from the 600 mL purge