Fuel Processing Technology 169 (2018) 226–235

Contents lists available at ScienceDirect

Fuel Processing Technology

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

Research article

Removal of NO in flue gas using vacuum ultraviolet light/ultrasound/chlorine in a VUV-US coupled reactor

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ARTICLE INFO

Keywords:
NO/SO_2
Integrated removal
Vacuum ultraviolet light/chlorine
Ultrasound
Hydroxyl radicals

ABSTRACT

Removal process of NO and integrated removal process of NO and SO_2 using vacuum ultraviolet light (VUV)/ultrasound (US)/chlorine system in a VUV-US coupled reactor were developed. The feasibility, key influencing factors and mechanism of removal process were investigated. The results reveal that SO_2 is almost completely removed in most experimental conditions due to its very high solubility and good reactivity. Addition of US enhances NO removal, and US of lower frequency is more effective than that of higher frequency. Vacuum ultraviolet light was found to be the most effective light source for removal of NO in VUV/US/chlorine system. Removal of NO was enhanced at a higher ClO^- concentration, light intensity, ultrasonic energy density or oxygen concentration, but was inhibited with the increase of NO, SO_2 or CO_2 concentration. Initial solution pH and reaction temperature were found to have double effect on NO removal. The key active species in different systems were detected, indicating that VUV/US/chlorine system had the highest hydroxyl radical yield. High oxygen concentration favors the generation of ozone. NO is mainly removed by oxidations of hydroxyl radical, ClO^- and $O\cdot/O_3$. Amplification of removal process were also discussed.

1. Introduction

SO_2 and NO_x emitted from fossil fuel combustion are the two main gaseous pollutants that cause acid rain and photochemical smog [1,2]. Apart from the direct damages caused by NO_x and SO_2, NO_x and SO_2 were also the precursors of $PM_{2.5}$ through a series of homogeneous and heterogeneous reactions [3,4]. According to the rough statistics, there are about > 800,000 small and medium coal-fired boilers and industrial furnaces in China's industrial and civil sectors [5]. The combustion consumption of coal from these small and medium-sized combustion equipments has exceeded one-third of total coal combustion consumption, which results in a huge air pollution because of the low-level combustion efficiency and lack of effective pollution control equipments.

In China, controlling of SO_2 and NO_x from coal-fired power station boilers has been effectively carried out by simultaneously installing independent desulfurization and denitrification devices (e.g., selective catalytic reduction (SCR) denitrification and wet flue gas desulfurization (WFGD) processes) [6]. However, this kind of hierarchical processing strategy for SO_2 and NO_x removal are not suitable for small and medium-sized combustion equipments due to complex systems and large installation space requirements. Some industrial furnaces even cannot install SCR denitrification technique due to the harsh restriction of process or technology [2,4]. Because of simple device and small space demand, integrated removal of SO_2 and NO_x from flue gas was recognized as a kind of very promising flue gas purification technology in the area of small and medium-sized combustion equipments [5].

In the past two decades, a variety of integrated removal technologies of SO_2 and NO_x from flue gas were developed. The most common ones mainly include catalytic oxidation, plasma removal, photochemical removal, ozone removal, adsorption removal, reduction absorption, complex absorption, conventional oxidation-absorption, radical oxidation-absorption, etc. [1–16]. These techniques have shown good prospects in the laboratory or pilot stage, but they cannot achieve large-scale industrial applications in a short time yet because of having one or more disadvantages in system reliability, investment and operating costs, secondary pollution, simultaneous removal efficiency of multi-pollutants, etc. Hence, developing new and more efficient integrated removal technologies of SO_2 and NO_x has important scientific significance.

Ultraviolet light-activated H_2O_2 and persulfate advanced oxidation technologies have been used to remove the air pollutants SO_2, NO_x and Hg^0 from flue gas [5,6,17–19], which have shown a good prospect because of several advantages such as efficient multi-pollutants removal

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http://dx.doi.org/10.1016/j.fuproc.2017.10.011
Received 14 July 2017; Received in revised form 11 October 2017; Accepted 11 October 2017

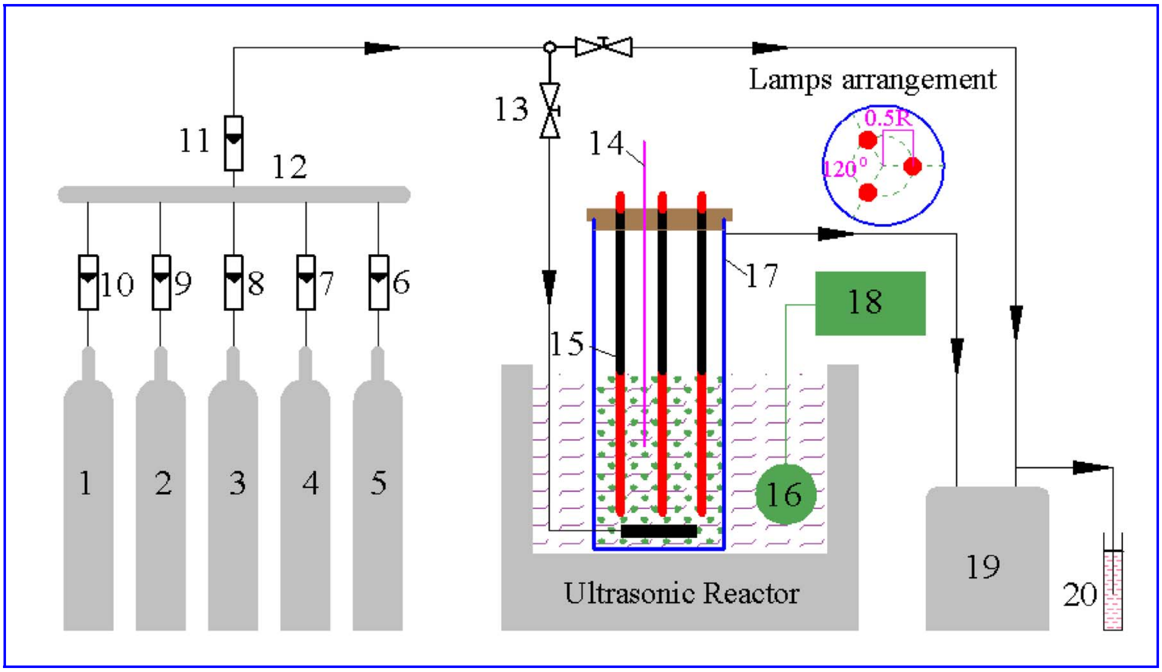

Fig. 1. Schematic diagram of experimental device.
1–5. cylinder gases; 6–11. flowmeters; 12. gas mixer; 13. gas valve; 14. thermometer; 15. UV lamp; 16. cooling coil; 17. silicate glass reactor; 18. refrigeration device; 19. coal-fired flue gas analyzer; 20. exhaust post-processor.

capacity and green environmental removal process. However, our studies [5,6,18,19] also show that this technology has the following two shortcomings, which hinder its application: (1) both of H_2O_2 and persulfate have high prices, resulting in high application cost; (2) In the actual flue gas and water, a variety of dust, impurities or dirt are always present. With the removal process, these dust, impurities or dirt will attach to the surface of quartz tubes, and hinder the effective transmission of ultraviolet light, which may lead to the failure of photochemical removal process.

Some studies [20–23] recently have shown that ultraviolet light can also activate hypochlorite (ClO^-) to produce free radicals to oxidize organic pollutants in wastewater. In China, both sodium hypochlorite and calcium hypochlorite are the by-products of production process in chemical/electrolysis, food/papermaking and disinfection/medical industries, and the output or production is very large [24]. The containing-hypochlorite wastewater will cause secondary pollution if they are directly discharged. Adding additional post-processing process for containing-hypochlorite wastewater will produce high post-processing costs. Based on the above situations, we propose to use containing-hypochlorite wastewater to replace peroxides, and to produce free radicals to oxidize SO_2 and NO_x in flue gas. This new technology not only can greatly reduce the application costs of UV activation technologies, but also can greatly reduce the post-processing costs of those enterprises that produce hypochlorite wastewater.

In recent years, ultrasonic technology has been widely used in the degradation of organic pollutants in wastewater, synthetic industry and cleaning industries [25–29]. Considering the contamination problem of UV lamp quartz tube surface, we propose to add ultrasonic cavitation in the reaction solution to keep the surface of quartz tubes clean. As a new coupling process, studying the additional effects of ultrasonic cavitation on removal process is indispensable (in fact, ultrasonic cavitation has been confirmed to have impact on chemical and mass transfer processes [28,29]). In addition, our previous results [5,6,17,19] mostly used shortwave ultraviolet light of 254 nm to produce free radicals to oxidize SO_2, NO_x and Hg^0. However, shortwave ultraviolet light of 254 nm cannot excite O_2 and H_2O to produce reactive species O_3, $\cdot O$ and $\cdot OH$ (both O_2 and H_2O are the main components of flue gas and solution, which are also good free radical sources). The present results from the Fig. 2(a) show that under the same experimental conditions, vacuum ultraviolet light of 185 nm has higher NO removal efficiency than shortwave ultraviolet light of 254 nm. Hence, the vacuum ultraviolet light of 185 nm will be used as an excitation light source of the photochemical reaction in this work.

Based on the above several ideas and technical routes, we develop novel process on removal of NO and integrated removal of NO and SO_2 in flue gas using vacuum ultraviolet light (VUV)/ultrasound (US)/chlorine system in a VUV-US coupled reactor, and to investigative several key fundamental issues in the removal process of NO_x and SO_2. These key fundamental issues are as follows: (1) to examine the feasibility on NO_x and SO_2 integrated removal using VUV/US/chlorine system in VUV-US coupled reactor; (2) to investigate the effects of key influencing factors, including light wavelength, light intensity, ultrasonic energy density, ultrasonic frequency, ClO^- concentration, reaction temperature, initial solution pH and $O_2/NO/SO_2/CO_2$ concentrations, on NO and SO_2 removal; (3) to detect the reaction products and to reveal the removal mechanism. The results will provide important theoretical basis for the follow up research and applications of this new removal technology.

2. Experimental section

2.1. Experimental device

The experimental device mainly includes a simulated flue gas generating device consisting of five cylinder gases ($NO/SO_2/O_2/N_2/CO_2$), six flowmeters and a gas mixer, a measuring and post-processing device