Effect of the molecular structure of nitrogen compounds on the pollutant formation in a bubbling fluidized-bed combustor

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ABSTRACT

To investigate the effect of the molecular structure of nitrogen compounds on the CO and NO emissions from experiments conducted in a bench-scale BFBC (bubbling fluidized-bed combustor), feed materials are prepared by mixing the model compounds (including pyridine, pyrrole, quinolone, aniline, nitrobenzene, 1-naphthylamine, urea, and arginine) with activated carbon to keep the overall nitrogen content at 1.5 wt% because this value is near the median of nitrogen content range ($0.5 - 2.5$ wt%) in most coals. The "de-NO" ratios for the combustion of various nitrogen compounds within the freeboard have been studied. Effects of bed temperature and additional water on the pollution emissions were also investigated. Experimental results show that the major factors for CO and NO formation, from the combustion of model compounds, were the molecular structure and functional groups, respectively. NO emission and it conversion both increased at first and then decreased with increasing bed temperature. Aromatic compounds have the highest fuel nitrogen (fuel-N) conversion to NO_x in the combustor chamber, followed by heterocyclic and amine compounds. CO and unburned char have significant effect on NO reduction in the freeboard. Controlling the additional moisture content in the feed material is a promising method for reducing NO emissions.

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1. Introduction

Fluidized-bed combustion has gained popularity in the 1990s, especially because of its low pollutant emissions. Previous research has shown that the adsorption of SO_2 could be effectively resolved using limestone. At the same time, numerous researchers have investigated the mechanism of NO_x formation and reduction in fluidized bed combustion. In FBC (fluidized bed combustion), the mechanism of NO_x formation and reduction are quite complex and difficult to correlate with the variances in NO_x emissions under various operating conditions.

The formation of thermal NO_x and prompt NO_x at low temperatures, 750–900 °C, is negligible in FBC. The conversion of fuel-N to NO_x is believed to arise through intermediates, such as HCN HCN (hydrogen cyanide) and NH_3 (ammonia), the main path for NO_x formation in FBCs.

As solid fuels such as coal and biomass or sludge enter the combustor chamber, the pyrolysis takes place first. Then, part of the fuel nitrogen (i.e. fuel-N) releases as volatile-N, including tar-N, HCN, and NH_3, while some nitrogen and carbon remains in the char. Subsequent oxidation of these nitrogen species releases NO and N_2O as nitrogen oxide pollutants. Because the breakdown of fuel-N into volatile-N and char-N in pyrolysis is one of the key steps for the formation of NO and N_2O [1], the behavior of fuel-N in pyrolysis has been studied extensively using various types of reactors and fuels under different conditions [2].

Coals generally contain $0.5 - 2.5$ wt% nitrogen [3–5] and consist of a complex mixture of aromatic hydrocarbons and heterocyclic aromatic compounds. Chemically bound nitrogen in coal and coal-derived fuels is known to occur predominantly in the form of heterocyclic compounds with pyrrolic and pyridinic structures [6–9]. The presence of quaternary nitrogen is also observed, but the nature of the quaternary nitrogen is not clear [10]. The pyrrolic, pyridinic, and quaternary nitrogen typically account for 50–80%, 20–40%, and 0–20% [7], respectively, of the total nitrogen content of coal. A wide range of nitrogen compounds has been used to simulate volatile-N behavior in combustion. For coal-type fuels, several summaries of the fuel characterization work are available [2,11]. Hansson et al. [4] found that the distribution of nitrogenous

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species in the pyrolysate of model substances and bark depend significantly on the fuel's nitrogen functionalities.

Cyanoacetylene (HCCCN) has been reported to be the principal nitrogen intermediate [3] that converts rapidly into HCN at high temperatures. Other major products are acetylene (C_2H_2) and hydrogen (H_2). Nitriles, which contain the −CN group, could be expected to yield large amounts of HCN, but this expectation is not supported by any available data. During the combustion of model compounds that contain oxygen functional groups such as hydroxyl and carboxyl or carbonyl groups in the FBC, NH_3 is the main intermediate [12,13]. The ratio of NH_3 to HCN is influenced by the oxygen functionality and its position relative to nitrogen in the molecule. The OH groups bound directly into the ring structure increase the conversion of nitrogen to NH_3 [13].

Most previous studies, related to the mechanism of NO_x emission from combustion using model compounds, are focused primarily on the formation of NO_x predecessors. However, there are some differences among their conclusions. Besides, in most studies, CO emission from combustion of different fuels is considered to be a function of operating parameters such as bed temperature, excess air ratio, superficial velocity, etc.

Relatively few studies have addressed the effect of molecular structure of model compounds on CO emissions.

CO and NO, the main pollutant emissions of FBC, have regulatory emission limits in most countries [14]. This motivates our interest in identifying the relationships between the fuel-N and the pollutant emissions from fluidized bed combustion.

The purpose of this work is to improve the understanding of the effect of the molecular structure of nitrogen compounds on CO and NO emissions during combustion in BFBC (bench-scale bubbling fluidized-bed combustor). In this study, the model compounds are used to examine the effect of the nitrogen functionality on the fuel-N conversion and the de-NO ratio in the freeboard. These model compounds represent the common types of fuel nitrogen bonds found in fossil fuels and biomass. The feed material is prepared by mixing eight nitrogen model compounds with pure AC (activated carbon) to maintain the overall nitrogen content. Meanwhile, the effects of bed temperature and additional moisture on the CO and NO formation are investigated.

2. Experimental section

2.1. Materials

For this study, the pyridine, pyrrole, quinoline, nitrobenzene, aniline, 1-naphthylamine, urea, and arginine (a total of eight nitrogen-containing compounds) were selected to simulate the
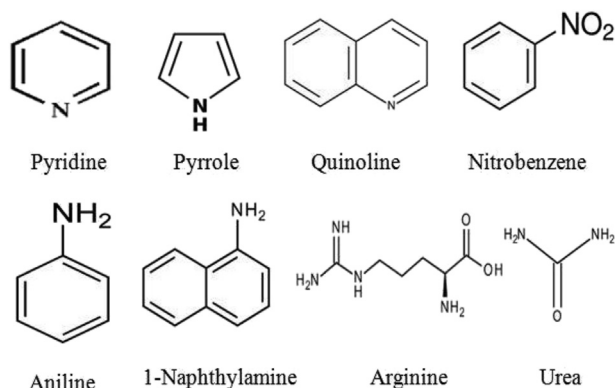

Fig. 1. The chemical structure formulas of model compounds.

nitrogen functionalities in fuels, as shown in Fig. 1. The material properties of eight model compounds were given in Table 1. These eight model compounds contain five types of nitrogen functionalities. The five nitrogen functionalities, pyrrolic, pyridinic, amino, amine and nitro groups, were considered to play a significant role in the conversion of fuel-N to NO. The model compounds were obtained from Uni-onward Corp., Echo Chemical Co., Ltd., and Merck Millipore Taiwan, LTD.

Excluding 1-naphthylamine, urea, and arginine, the other five model compounds are found in liquid form. The feed materials were prepared by mixing each liquid compound with pure AC, and the overall nitrogen content was fixed at 1.50 wt%. The solid compounds were dissolved in deionized water to mix with pure AC.

To minimize the effect of the carrier on NO emissions, pure AC of low nitrogen content (0.56%) was selected for this study. The properties of pure AC were given in Table 2. AC is obtained from China Activated Carbon Industries, Ltd. Silica sand (99.5%, SiO_2 and 0.5% Al_2O_3), with a mean diameter of 0.54 mm and an apparent density of 2500 kg/m³, was used as the bed material in this study, and the particle voidage of bed material was 0.40.

Before mixing with the model compounds, raw AC was crushed into small pieces and then was sieved to 2.8–4 mm. The sieved AC was oven-dried at 120 °C for more than 1 h, followed by cooling down to 30 °C before being sent to a tumbler mixer. The capacity of this tumbler mixer was 15 kg per batch. Nitrogen model compounds were injected into the mixer via a syringe while the mixer was rotating. Approximately one hour was required to inject the model compounds into the mixer. The tumbler mixer was operated at a speed of 30 rounds per minute for 12 hours before the feed material was prepared.

2.2. Experimental setup

All of the tests are conducted in a bench scale bubbling fluidized bed combustion system which includes the combustor chamber, feed system, air supply system, electrical heating system, and flue gas treatment system [15]. The schematic diagram of the bubbling fluidized bed combustion system used in this study is shown in Fig. 2.

The cross-section of the combustor chamber is 0.22×0.11 m², and its height is 0.678 m. The open area ratio of the distributor is 0.52%. The freeboard section is fabricated by using an SUS310 pipe with an inner diameter of 0.154 m and a height of 4.0 m. The combustor chamber and freeboard are equipped with an electrical heating facility and wrapped with 0.025 m thick ceramic fiber for thermal isolation. The feeding system is an assembly of a feedstock hopper and a screw feeder, and the feeding point is 0.5 m above the distributor.

At the beginning of the start, the combustor chamber is preheated using electrical heating facility, and the secondary air is continuously injected into the freeboard. Primary air is injected into the combustor occasionally to stir the sand. The feed material is fed into the combustor via a screw feeder after the bed temperature reaches 500 °C, and the flow rate of primary air is increased gradually. The temperature of the combustor is controlled by an automatic control system to maintain the reactor at a fixed temperature. Approximately 3–5 h is required for the system to reach steady state. The primary air and secondary air is supplied by an NCS-100 air compressor. In addition, a nitrogen supply system is used to inject nitrogen into the primary air to maintain the gas velocity at a constant value. Four equally spaced secondary air injection nozzles 0.013 m in diameter are installed tangentially at 0.796 m above the distributor. The flue gas which generated from the combustor passes through a cyclone to remove most of the fly ash including unburned char and small ash particles. Afterward, the