



Research article

NO reduction by different tar agents and model compounds in a drop-tube reactor

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ABSTRACT

Our previous studies suggested that the biomass tar derived from pyrolysis of distilled spirit lees (DSL) is an attractive agent for lowering NO_x emission in the circulating fluidized bed decoupling combustion (CFBDC) process. The present work is furthered to evaluate the capabilities of other tar agents including sawdust (SD) tar and Xianfeng (XF) coal tar for NO reduction in a lab-scale drop-tube reactor. Additionally, five representative model tar compounds including phenol, benzene, acetic acid, methyl acetate and heptane were also tested to clarify the contribution of the main components in tar agents to NO reduction. The realized NO reduction efficiency by tar obviously varied with the reburning stoichiometric ratio (SR) and reaction temperature. At a specified mass feeding rate of reductant, say 0.15 g/min, the NO reduction realized by the SD tar is higher than that by the XF coal tar, and was even better than that by the DSL tar obtained in our previous study. Testing the NO reduction by model tar compounds revealed that phenol plays an important role in enabling its good NO reduction for the SD tar. The major understanding from the work is that the compounds containing at least an aromatic ring (e.g. phenol, benzene, etc.) are the major contributor for reducing NO in either biomass tar or coal tar.

1. Introduction

Nitrogen oxides (NO_x) from fuel combustion not only injures human health but also forms acid rain and photochemical smog [1,2]. Several technologies have been developed to reduce NO_x emission during fuel combustion, the priority way of combustion NO_x control. Our previous work shown that the so-called circulating fluidized bed decoupling combustion (CFBDC) is a low-NO_x combustion technology that has been well proven to be effective in lowering at least 50% NO_x formation comparing to other traditional combustion technologies [3–5]. The decoupling combustion technology separates the combustion process into drying/pyrolysis of fuel and combustion of char and volatile products consisting of non-condensable pyrolysis gas and condensable tar. In CFBDC, the pyrolysis-generated volatile is sent to an intermediate position of the char combustor to allow for its co-burning with char. The co-burning of fuel pyrolysis products in such an intermediate position could be considered as a reburning way that can effectively reduce the NO_x formed by burning char in the bottom of the combustor.

Fuel reburning is a well-known low-NO_x combustion technique. Injecting the reburning fuel into the reburning zone establishes actually

a fuel-rich atmosphere where fuel is decomposed to release some reactive species. The NO_x formed in a primary combustion zone with excessive air then can be reduced by such reactive species to form N₂ [6–10]. In CFBDC, the reduction of NO_x involves the effects of all pyrolysis products including char, tar and pyrolysis gas (non-condensable). In recent years, lots of studies have demonstrated the significant effect of char [11–13] and reducing gas [14–16] on NO_x reduction in reburning process, but there were very few studies on the NO_x reduction by tar. Luo et al. [17–20] revealed that the tar components are highly helpful in increasing the NO reduction efficiency. The tar derived from fuel pyrolysis is composed of many aromatic species including phenols, BTX and other compounds such as aliphatic, carboxylic acid and ester groups [21]. At high temperatures, the decomposition of these species releases some hydrocarbon and non-hydrocarbon species like CH₃ and HCCO radicals, CO and H₂ gaseous [22,23], which are well-known to be the important intermediates for NO_x reduction reactions [14,16,24].

In our previous studies [25,26], we found that the tar derived from pyrolysis of distilled spirit lees (DSL) is an efficient agent for lowering NO_x emission in the CFBDC system. With the aim of further

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understanding the mechanism of low-NO_x emission in CFBDC treating different fuels, this study is devoted to revealing the characteristics of NO reduction by different tar agents. Sawdust and coal were selected to obtain the tars used in evaluating NO reduction, and the results were also compared with that realized using the DSL-derived tar through our previous work [25]. In addition, the NO reduction efficiencies realized by five representative model tar compounds were also further evaluated to understand the different NO reductions for different tars and to figure out the contributions of different agents to the achieved NO reduction in reburning.

2. Experimental

2.1. Tar preparation and properties

The NO reduction agent tested in this study included tars derived from pyrolysis of sawdust (SD) and Xianfeng (XF) coal in a nitrogen fixed-bed reactor at 500 °C for 30 min. The tar was collected via a condenser at 5 °C and further dehydrated over anhydrous MgSO₄. The temperature 500 °C is quite close to the those adopted for fuel pyrolysis in CFBDC and it also guarantees the higher yield and diversified composition of the prepared tar. At other higher temperatures, the tar would be mainly heavy components. Table 1 shows the results of ultimate analysis for the tar agents obtained. The chemical composition was obtained using a GC–MS spectrometer (Shimadzu QP 2010 Ultra). In Fig. S1 of Supplementary data we presented the original GC–MS spectra of all used tar samples. The content of each component refers to the percentage of its peak area, say, the proportion of each peak area to the total area of all peaks in a GC–MS spectrum. The identified compounds in tar were further divided into some functional groups, as detailed in Table S1 of Supplementary data. Their content (area) percentages were listed in Table 2 (the total area for each group over the total area of all peaks). Obviously, phenols, acids and ester are the major components of biomass tars, whereas aromatics and aliphatic hydrocarbons are the major components of coal tar. Consequently, in this study we adopted phenol, acetic acid, methyl acetate, heptane, and benzene as the model compounds of the tested tars to further evaluate the NO reductions realized by individual chemical compounds containing in the tars.

2.2. Apparatus and method for testing NO reduction

An experimental drop-tube reactor (DTR) system was adopted in testing NO reduction, which was also described in our previous work studying the NO reduction by DSL pyrolysis products [25]. Fig. 1 shows that the system consists of a reaction zone, a simulated flue gas supplying system, a NO reductant feeding system and a flue gas analysis system. The reaction zone of the DTR was made with a corundum tube of 100 mm in inner diameter and 1680 mm in length, which was heated by an external electric furnace to allow reaction temperatures of up to 1550 °C.

The experiments were performed on the same experimental conditions as in our previous work [25]. The simulated flue gas consisted of 800 ppmv NO with varied concentrations of O₂ and balanced contents of N₂. The total flow rate of flue gas for experiments was 45 L/min

Table 1
Ultimate analyses of used tar agents.

Sample	Ultimate analysis (wt%, on dry basis)			
	C	H	N	S + O ^a
SD tar	63.65	6.81	2.36	27.18
DSL tar [25]	71.32	7.09	5.16	16.43
XF coal tar	72.09	5.96	1.08	20.92

^a By difference.

Table 2
Composition analyses of used tar agents (based on GC–MS results).

Group of components	Composition (% area)			Representative reagents
	SD tar	DSL tar [25]	XF coal tar	
Acid	3.25	13.99	–	Acetic acid
Ester	1.93	25.21	–	Methyl acetate
Aliphatic	0.74	4.05	37.20	Heptane
Aromatic	3.623	5.61	55.59	Benzene
Furans	12.43	5.29	1.86	–
Hydroxyl	3.64	4.12	–	–
Ketone	7.74	1.53	–	–
Phenols	66.71	40.16	5.47	Phenol

(STP). Once all parameters according to the set conditions reached their steady states in the DTR, the tar reductant with feeding rate of 0.15 g/min was fed continuously into the reactor with 4 L/min (STP) of N₂ as its carrier gas to start the reduction of NO containing in the simulated flue gas. The reductant feeding system had a metering pump for tar, which was carefully calibrated before each experiment. Table 3 summarizes the typical experimental conditions adopted in this study. In the table, the stoichiometric ratio (SR) for reburning refers to the ratio of the adopted O₂ flow rate in experiment to the O₂ flow rate required for stoichiometric combustion of the NO reduction reactant (tar) fed into the reactor. Thus, the conditions of SR < 1.0 and SR > 1.0 can be viewed as fuel-rich and fuel-lean conditions, respectively. The variation of the reburning SR for a tested tar reductant was achieved by adjusting the O₂ concentration in the simulated flue gas.

The concentrations of NO, CO, and O₂ in the outlet gas from the DTR were continually monitored using an online gas analyzer (SDL M3080, Beijing SDL Technology, China). It was confirmed that the N₂O and NO₂ concentrations in the sampled gas were below 10 ppm so that only the NO reduction efficiency was evaluated. The NO reduction efficiency (%) was defined as

$$\eta = \left(1 - \frac{[\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \right) \times 100\%, \quad (1)$$

where η is the NO reduction efficiency (%), $[\text{NO}]_{\text{in}}$ is the NO concentration (ppmv) at the inlet of reburning zone (included the dilution effect by adding carrier gas), and $[\text{NO}]_{\text{out}}$ is the NO concentration (ppmv) measured at the outlet of reactor. This means that the gas volume variation through the reactor was neglected in estimating the NO reduction efficiency according to the measured NO concentrations.

3. Results and discussion

3.1. NO reduction by tar agents

Following the previous studies [6,12,17,25], the reburning SR is further considered as a key parameter in evaluation of the NO reduction by tars. Fig. 2 presents the variations of NO reduction efficiencies (η) with SR at reaction temperatures of 800, 900, and 1000 °C for both SD tar and XF coal tar agents. The results obtained in our previous work [25] for DSL tar agent were also shown to make an effective comparison. Generally, the achieved trends of NO reductions by the SD tar and XF coal tar agents are similar to that by the DSL tar agent, which first increase and then decrease with the rise of SR. Also, the NO reduction efficiency evidently increased with raising reaction temperature for all the compared tar agents. However, different temperatures caused more or less different variations of NO reduction with SR. Indeed, the NO reduction efficiencies by all tar agents tended to reach their maximal values at lower SR when the reaction temperature was raised to 900 or 1000 °C. This phenomenon was attributed to the competition between the reactions of tar agent with NO and oxygen, which was previously

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