

# Experimental investigation of NO<sub>x</sub> emission and ash-related issues in ammonia/coal/biomass co-combustion in a 25-kW down-fired furnace

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## Abstract

Co-firing ammonia in coal units is a promising approach for the phasedown of coal power. In this paper, we demonstrate the feasibility of burning ammonia with coal and biomass in a 25- kW down-fired furnace with a swirl-stabilized burner. Ammonia is injected from the central tube at thermal ratios ranging from 0 to 30% and can be completely burnt out in most co-firing cases. We investigate the NO<sub>x</sub> emission, unburnt carbon in fly ash, particulate matter formation and ash deposition behaviors when co-firing NH<sub>3</sub> with either SH lignite coal or the coal/biomass blend. With a fixed air staging ratio, the NO<sub>x</sub> emission increases linearly with the NH<sub>3</sub> fuel ratio. By increasing the percentage of secondary air, the emitted NO<sub>x</sub> can be reduced to 300 ppm with an NH<sub>3</sub> thermal ratio of 30%. The unburnt carbon is affected by NH<sub>3</sub> addition in a complex manner. With a 30% (thermal) NH<sub>3</sub> addition, the unburnt carbon increases from 0.4% to 5.6% for the SH coal mainly due to a temperature drop, but decreases from 2.2% to 0.7% for the SH coal/biomass blend. As for the ash-related issues, the addition of NH<sub>3</sub> to either coal or coal/biomass blend is found to alleviate both the fouling intensity and the ultrafine particulate matter formation ability. This is a major advantage over biomass combustion.

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*Keywords:* Ammonia/coal/biomass; Co-combustion; NO<sub>x</sub> emission; Air staging ratio; Ash formation and deposition

## 1. Introduction

There is a worldwide consensus on the phase-down of unabated coal power to reduce carbon emission [1]. The year 2020 sees a plummet by 5% from 2019 levels in the global coal demand [2], but

coal still provides 27.2%, the second-largest ratio, of the world's primary energy consumption [3]. In many developing countries the ratio is even higher (e.g., China 56.6%, India 54.8%, Vietnam 51.4%, Indonesia 40.2%, 2020) [3]. Besides, the output of thermal power can be controlled actively and flexibly to stabilize the grid with a rapidly growing penetration of intermittent renewables [4]. Indeed, coal power in developing countries like China has been playing the role of peak shaving for years [4]. Therefore, instead of shutting down the existing units,

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switching to carbon-neutral fuels is believed as a more economical and environmentally-benign approach.

Ammonia ( $\text{NH}_3$ ) and biomass are among the most promising candidates for this purpose. Co-firing biomass with coal has been widely studied and used especially in Europe [5]. In China, some coal plants are retrofitted for co-firing biomass ( $\leq 10\%$  of the full power) but frequently run with greater fuel ratios of biomass at reduced outputs. However, the availability issue limits the biomass usage scale, and the severe fouling propensity in biomass combustion remains challenging [6,7].

$\text{NH}_3$ , by contrast, obtains more and more attention recently for its great potential as a large-scale and long-duration energy carrier. Now,  $\text{NH}_3$  is gradually becoming an indispensable portion of the hydrogen industry with mature technology of global transport and storage at scale [8,9]. Burning  $\text{NH}_3$  in coal plants relies on  $\text{NH}_3$  costs and combustion technology. The electricity cost of co-firing coal with 20%  $\text{NH}_3$  (thermal input) is projected as 150 USD/MWh (China, without CCS, our own estimation) and 180 USD/MWh (Japan, with CCUS), which is compared with 167 USD/MWh (Japan) and 228 USD/MWh (Europe) for coal power equipped with CCUS [10,11].

With a cost-competitive prospect, co-firing  $\text{NH}_3$ -coal has been tested on a 1.2 MW furnace ( $\text{NH}_3$  fuel ratio from 0 to 100% with various feeding modes) [12] and a 155 MW boiler ( $\text{NH}_3$  fuel ratio 0.6%) [13]. Generally, little  $\text{NH}_3$  slip is detected, and the  $\text{NO}_x$  emission is increased to a mild extent with the  $\text{NH}_3$  fuel ratio no greater than 20%. The same trend is observed in a numerical study on the full-scale furnace [14]. These efforts alleviate the  $\text{NO}_x$  concerns at least for co-firing  $\text{NH}_3$  with a small fuel ratio. As a common species for fuel-N transformation in pulverized coal combustion,  $\text{NH}_3$  itself is an effective  $\text{NO}$  reduction agent [15]. It is recently found that the  $\text{NH}_3$  co-firing synergistically promotes  $\text{NO}$  heterogeneous reduction with char [16]. Therefore, the key to control  $\text{NO}_x$  in an industrial  $\text{NH}_3$ -coal swirl flame seems to effectively 'trap'  $\text{NH}_3$  long enough in the volatile-rich region [8,9,12,17]. It must be achieved through elaborate manipulation of the fuel-air mixing strategy.

However, many issues on practical  $\text{NH}_3$ -solid fuel co-combustion remain controversial or unclear: First, little is known about the  $\text{NH}_3$  influence on mineral ash formation and deposition, the key factor affecting the safety of heating surfaces in the boiler. Secondly, as pointed out in Ref. [9], the reported unburned carbon fractions in fly ashes after  $\text{NH}_3$  addition seem to be inconsistent in the literature. Then, co-firing  $\text{NH}_3$  with biomass (or coal-biomass blends) has been rarely studied, even though it may as well become practical. Last, decision-makers of the coal plant may want to know about the limit of the unit to burn  $\text{NH}_3$  without any system retrofit.

We note that the 20~100-kW furnaces are well suited to fill the research gap because coal burns out with time-temperature histories and particle concentrations similar to those in practical boilers and the scale of these furnaces still allows precise and reproducible operating conditions for mechanistic studies [18–20]. Recent progress in simultaneous characterization of the fly ash and deposits [21–23], as well as the flexibility of the furnace to fuel types, makes it possible to delve into  $\text{NH}_3$ -coal/biomass co-combustion performance, but it has not been reported yet.

The objective of this work is to elucidate the combustion performance in co-firing  $\text{NH}_3$  with coal/biomass in a 25-kW quasi-one-dimensional self-sustained down-fired furnace. Ammonia is centrally fed into a swirl coal burner. A set of well-designed conditions are achieved to study: (i) ash-related issues; (ii)  $\text{NH}_3$ -coal-biomass co-combustion and the effects to, among others, the unburnt carbon; (iii) the limit of burning  $\text{NH}_3$  on conventional swirl burners with little structural retrofit. We reveal the  $\text{NO}_x$  emissions and unburned carbon in fly ashes under various  $\text{NH}_3$  fuel ratios (up to 30% thermal) and secondary air ratios. Ammonia slip is generally negligible. The fouling propensity and fine particle size distributions are reported for the first time in the  $\text{NH}_3$ -coal-biomass system.

## 2. Experimental apparatus and methods

### 2.1. Fuel property

In this work, we use SH lignite coal, the design coal of a 2000-MW unit located in the northwest of China. A corn straw (denoted CS) is chosen as the biomass to be mixed uniformly with coal. The thermal ratio of CS is set as 20% (higher than 10% to better mimic the real situation and further manifest the biomass effect), with the blend denoted SH:CS=4:1. Table 1 lists the fuel properties. Note that the blend has higher volatile and fewer ash contents than SH coal. Greater Na and K fractions are present in the blend, which may affect the ash behaviors [22,24–26]. Fig. 1 shows the volumetric particle size distributions of the raw fuel samples measured by a Malvern (Master sizer 2000). It is found that the mean size of CS is about 3 times of SH coal due to the weaker grindability of biomass. Table 2 lists the feed rates of SH and the blend in the experiments with the  $\text{NH}_3$  fuel ratios set as 0, 0.1, 0.2, and 0.3.

### 2.2. 25-kW down-fired furnace and sampling methods

The combustion experiments are performed in a 25-kW self-sustained, quasi-one-dimensional

Table 1  
Properties of SH lignite and the blend (SH: CS=4:1).

	SH	SH: CS=4:1
Proximate analysis (wt.%, dry basis)		
Fixed carbon	45.10	39.51
Volatile matter	32.96	42.99
Ash	21.94	17.50
HHV (MJ/kg)	19.30	18.66
Ultimate analysis (wt.%, dry, ash-free basis)		
C	50.49	48.42
H	4.12	4.34
N	0.88	0.82
S <sub>total</sub>	0.72	0.56
O (by difference)	43.85	45.86
ash composition (wt%)		
SiO <sub>2</sub>	39.62	38.41
Al <sub>2</sub> O <sub>3</sub>	16.29	14.70
Fe <sub>2</sub> O <sub>3</sub>	9.21	8.98
CaO	15.25	15.78
MgO	4.21	4.23
TiO <sub>2</sub>	0.95	0.98
SO <sub>3</sub>	9.35	9.32
P <sub>2</sub> O <sub>5</sub>	0.10	0.24
K <sub>2</sub> O	2.06	3.67
Na <sub>2</sub> O	1.73	1.87
d <sub>0.5</sub> (μm)	33.09	106.73

Table 2  
Feed rates of SH coal and the blend in the experiments.

NH <sub>3</sub> fuel ratio (thermal)	SH (kg/h)	SH: CS=4:1 (kg/h)	Overall air ratio
0.0	4.07	4.18	1.3
0.1	3.66	3.76	1.3
0.2	3.26	3.34	1.3
0.3	2.85	2.93	1.3

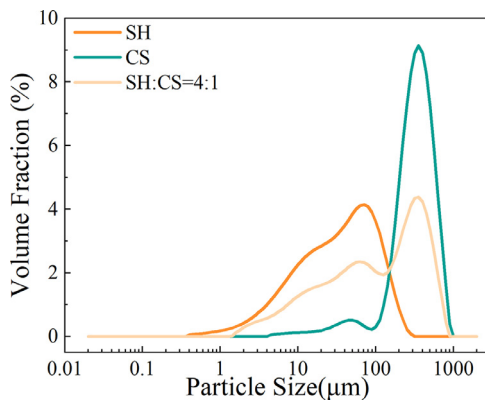


Fig. 1. Volumetric particle size distribution of SH lignite, CS biomass, and the blend (SH: CS=4:1).

down-fired furnace as exhibited in Fig. 2. The structure and operation procedures of the furnace are detailed in our previous work [20,22]. The refractory lining of the furnace is made of silicon carbide high-temperature ceramic, calcium silicate board

and aluminum silicate fiber felt. The inner diameter of the furnace is 150 mm. The total height is 3800 mm. The flue gas flows pass a treatment system before entering the stack. Four sampling ports denoted P1-P4 are designed for fly ash and deposit sampling, with the temperatures monitored by S-type thermocouples. In particular, the residence time in P4 (2660 mm away from the burner) is  $\sim 1.5$  s to ensure the fuel burnout. Before the experiments, the sealing of the furnace was carefully examined to prevent NH<sub>3</sub> leak.

A multi-fuel burner equipped on the furnace top is shown in Fig. 2a. The burner consists of four outside-in coaxial tubes, including the swirled secondary air preheated to 380 °C, the primary air carrying pulverized solid fuels (coal or biomass) to be fed into the furnace through the annular port, the liquefied petroleum gas (LPG) for warming up the furnace to be injected from annular-placed small holes, and the central tube for gaseous NH<sub>3</sub> injection. The NH<sub>3</sub> nozzle is fixed at 16 mm.

The flue gas compositions including NO<sub>x</sub> (NO, NO<sub>2</sub> and N<sub>2</sub>O), CO, CO<sub>2</sub>, O<sub>2</sub> and SO<sub>2</sub> are measured by two gas analyzers (MRU-VARIO PLUS)

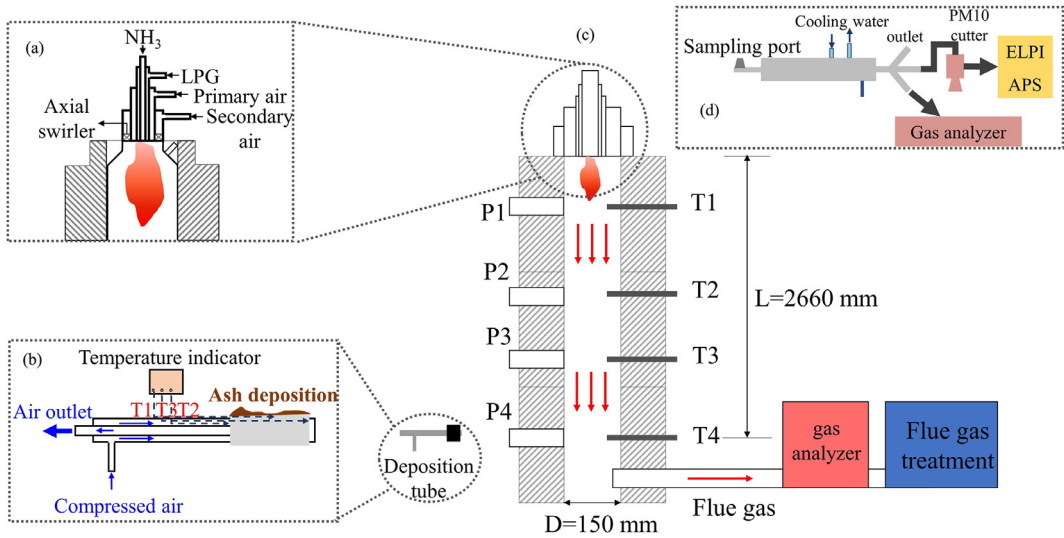


Fig. 2. Schematic of the 25-kW down-fired furnace: (a) The swirl burner adapted to central  $\text{NH}_3$  injection; (b) Deposition probe; (c) The furnace with sampling ports P1–P4 and temperature monitors T1–T4; (d) Fly ash sampling probe.

upstream of the gas treatment system (see Fig. 2c). The sampling lines are heated above  $120^\circ\text{C}$  to prevent water condensation and  $\text{NO}_2$  dissolution. Another analyzer (Gasetm DX4000) is used to measure ammonia slip at the outlet of the furnace.

The ash deposits and fly ash samples are collected at P4 of the furnace. The deposition probe (see Fig. 2b) has a removable sleeve of  $\Phi 20 \text{ mm} \times L 50 \text{ mm}$  with the surface temperature controlled at  $600^\circ\text{C}$  by compressed air. The sleeves are heated to  $900^\circ\text{C}$  before experiments to eliminate the oxidation-induced mass changes [20]. The sleeves are measured before and after deposition experiments for a certain elapsed time to record the deposited mass.

The fine particle sampling probe (see Fig. 2d) uses two stages of dilution to minimize the errors induced by the aspiration sampling [20]. The overall dilution ratio is  $\sim 150$  (using  $\text{CO}_2$  as the indicator). The particle size distributions are measured, respectively, by the APS (TSI Inc., aerodynamic diameter  $0.5\text{--}20 \mu\text{m}$ ) and ELPI+ (Dekati, aerodynamic diameter  $0.017\text{--}10 \mu\text{m}$ , under DLPI mode). The flue gas flows through a  $\text{PM}_{10+}$  cutter before entering ELPI+. The bulk ash trapped in the cutter is collected for TGA (TGA Q500) analysis to  $1000^\circ\text{C}$  to determine the unburned carbon.

In the experiments, a high-temperature-resistant camera is inserted into P2 to record the top flames, as shown in Fig. 3a for various fuels. The type I jet-like swirl flame [27] is formed in experiments (as shown in Fig. 3a, the flame is mainly located in the center of the furnace). The temperature profiles along the furnace are presented in Fig. 3b and are quite close among various fuels. The temperature at P4 is  $\sim 750^\circ\text{C}$ .

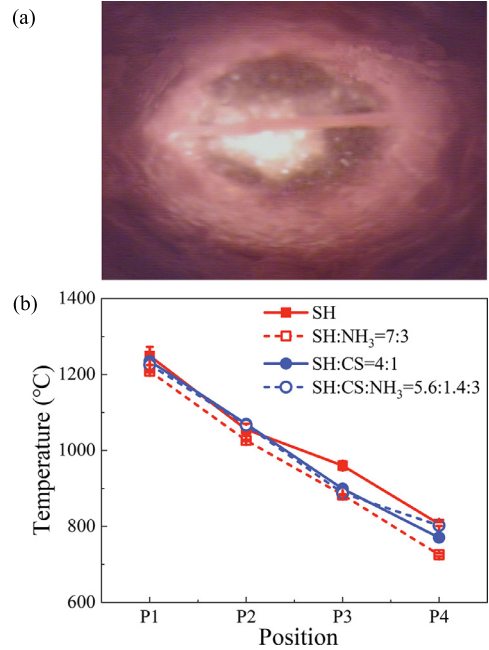


Fig. 3. (a) Typical top-view flame image (exposure time:  $1/2000\text{s}$ ); (b) Temperature profiles along the furnace for burning different fuels.

### 3. Results and discussion

#### 3.1. Ammonia slip and flue gas compositions from a continuous test

Fig. 4 presents the flue gas compositions during a series of fuel-switching operations in the furnace. LPG is first used to warm up the furnace to

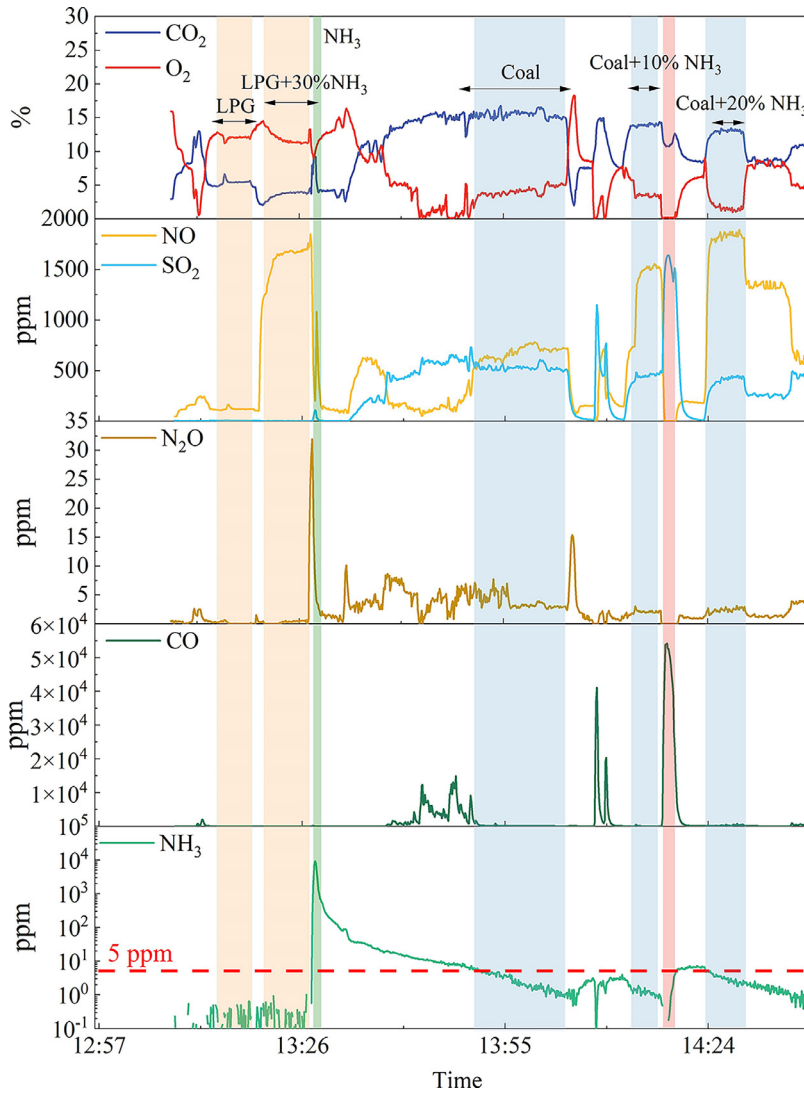


Fig. 4. Flue gas compositions during a series of continuous fuel switching operations.

reach stable conditions ( $\sim 1250^\circ\text{C}$  at P1), producing the flue gas NO about 100 ppm and almost no  $\text{SO}_2$ . Then we switch to co-firing LPG with 30%-thermal  $\text{NH}_3$ . Once ammonia is added, the  $\text{NO}_x$  emission largely increases to  $\sim 1700$  ppm. No ammonia slip is detected. We further test pure  $\text{NH}_3$  combustion by cutting down the LPG supply and increasing the  $\text{NH}_3$  flow rate to  $\sim 12$  kW. Unfortunately, this leads to a serious  $\text{NH}_3$  slip over  $10^4$  ppm and a NO emission  $\sim 1000$  ppm, which is lower than LPG+30% ammonia and results from the NO reduction by SNCR reactions with sufficient  $\text{NH}_3$  supply [8,28]. We have to cut off  $\text{NH}_3$  immediately and re-supply LPG until the monitored  $\text{NH}_3$  slip drops below 5 ppm. Then LPG is switched to pure SH coal, yielding flue gas  $\text{CO}_2$ ,  $\text{O}_2$ , NO,  $\text{SO}_2$  and

CO as  $\sim 16\%$ ,  $\sim 5\%$ ,  $\sim 700$  ppm,  $\sim 500$  ppm and  $\sim 100$  ppm, respectively. Further increasing  $\text{NH}_3$  fuel ratio to 20% results in even lower  $\text{CO}_2$  and  $\text{SO}_2$ , and NO increases to  $\sim 1800$  ppm. The ammonia slip is always less than 5 ppm in co-firing  $\text{NH}_3$ -coal, verifying that  $\text{NH}_3$  slip may not be a serious concern [14,29]. But the NO issue is vital.

Besides, the potent greenhouse gas nitrous oxide ( $\text{N}_2\text{O}$ ) can be formed from ammonia combustion [8,9]. As shown in Fig. 4, when cofiring  $\text{NH}_3$  with LPG or coal, flue gas  $\text{N}_2\text{O}$  is no higher than 2.5 ppm, far lower than NO ( $\sim 1500$  ppm). During pure  $\text{NH}_3$  combustion test, though, a notable  $\text{N}_2\text{O}$  emission ( $\sim 30$  ppm) is recorded along with the serious ammonia slip, which indicates that  $\text{N}_2\text{O}$  can be an issue of concern. No direct correlations can be



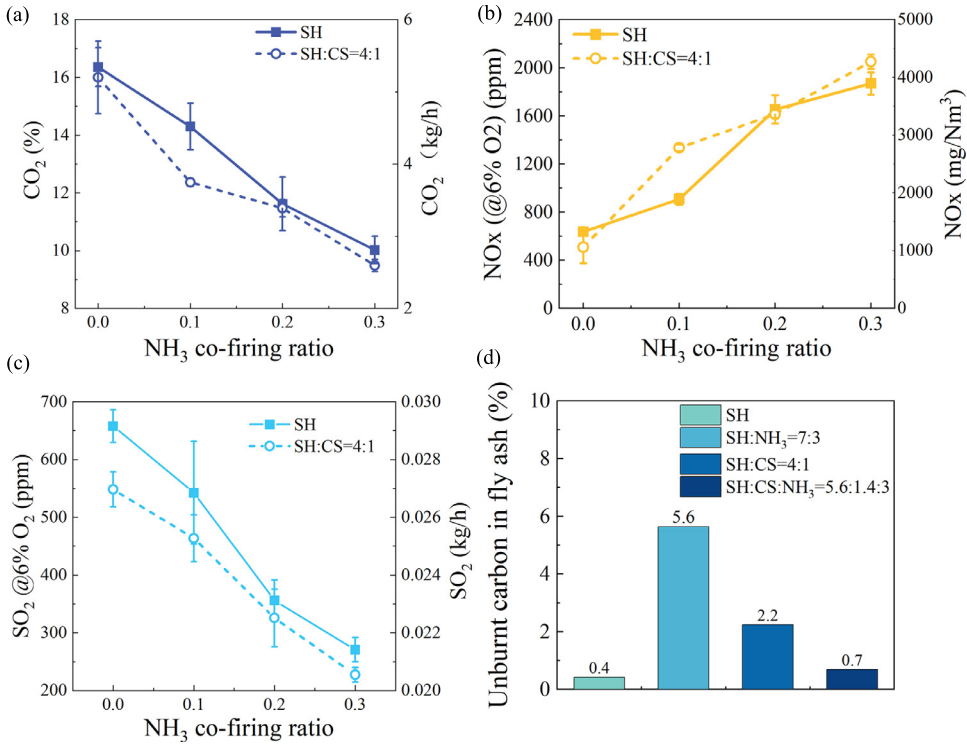


Fig. 5. CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> emission and unburnt carbon in the fly ash at different ammonia co-firing ratios.

inferred between N<sub>2</sub>O and NO (or O<sub>2</sub>, NH<sub>3</sub>, etc.) concentrations from the data. The N<sub>2</sub>O formation mechanism and its greenhouse effect in NH<sub>3</sub> combustion thus demand further research efforts.

### 3.2. CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> emission, and unburnt carbon in fly ash

Fig. 5 illustrates the measured CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> emission and unburnt carbon in the fly ash. To exclude the dilution effect, we calculate the mass emission rates (kg/h) of CO<sub>2</sub> and SO<sub>2</sub> based on the flue gas flow rates and the gas compositions. Because NH<sub>3</sub> is free of carbon and sulfur, the measured CO<sub>2</sub> (Fig. 5a) and SO<sub>2</sub> (Fig. 5c) emissions decline linearly with the NH<sub>3</sub> co-firing ratio for both SH coal and the blend (SH:CS=4:1). It highlights the positive effects of co-firing ammonia on carbon reduction. In addition, the blend (SH:CS=4:1) produces less SO<sub>2</sub> emission than pure SH coal combustion because the biomass CS has a lower sulfur content (see Table 1).

In contrast, the NO<sub>x</sub> emission in Fig. 5b increases almost linearly with the NH<sub>3</sub> co-firing ratio for both SH coal and the blend (SH:CS=4:1), provided that the air staging strategy and the excess O<sub>2</sub> concentration are kept the same. Recall that we have jet-like swirl flames in the experiments (Fig. 3a) and NH<sub>3</sub> was fed in as a central jet. There-

fore, the higher blending ratio of NH<sub>3</sub> leads to larger central fuel jet intensities and reduces the residence time of NH<sub>3</sub> in the fuel rich zone. With less extents of decomposition, NH<sub>3</sub> experiences a quicker entry into the oxidation zone where the fuel-N conversion into NO becomes active. It suggests the challenge the fuel-N in NH<sub>3</sub> poses to existing combustion facilities. For instance, our 25-kW furnace, without considerable modification of the burner, can only adopt an NH<sub>3</sub> co-firing ratio no greater than 10% with SH coal to ensure a flue gas NO<sub>x</sub> ≤ 1000 ppm, a concentration that can be effectively handled by current SCR systems.

We further characterize the unburnt carbon in the fly ash at sampling P4 in cases of 30%-thermal NH<sub>3</sub>, with results shown in Fig. 5d. For SH coal, a 30%-thermal NH<sub>3</sub> addition increases the fraction of unburnt carbon in the fly ash from 0.4% to 5.6%. The blend (SH:CS=4:1) features a larger value (2.2%) of unburnt carbon than pure SH coal, which can be interpreted by the much coarser particles of biomass CS (see Fig. 1). However, a 30%-thermal NH<sub>3</sub> addition to the blend reduces the unburnt carbon to 0.7%, though still larger than that of SH coal. While several previous studies report inconsistent results of NH<sub>3</sub> effect on coal burnout [12,14,17,29], our work reveals opposite trends from a single set of experiments burning different fuels, demonstrating that several factors with

distinct consequences should be taken into consideration.

As compared with pure SH coal, adding 30%-thermal  $\text{NH}_3$  may substantially reduce the temperature. The adiabatic flame temperature of  $\text{NH}_3$  ( $\sim 1800^\circ\text{C}$  [8]) is far lower than the burning temperature of coal/char ( $\sim 2000\text{--}2400^\circ\text{C}$  [30]). Moreover, the previous study shows that when  $\text{NH}_3$  co-firing ratio reaches 20% (thermal), the flame zone (FZ) temperature drops about  $200^\circ\text{C}$ , whereas the post flame temperatures drop about  $50^\circ\text{C}$  [14]. Hence, it is believed that with  $\text{NH}_3$  addition, the temperature difference in the flame zone (even upstream of P1) is remarkably greater than the  $40\text{--}100^\circ\text{C}$  shown in Fig. 3b. Besides,  $\text{NH}_3$  combustion could be more efficient in consuming oxygen and slows down the coal/char oxidation in flame zone. Both factors contribute to the increased unburnt carbon fraction for  $\text{NH}_3$ -SH coal co-combustion.

For the blend (SH: CS=4:1),  $\text{NH}_3$  co-firing from the central jet is likely to reduce the concentration of larger fuel particles and promote the mixing of solid fuel particles with combustion air, resulting in the improved burnout under the fixed air staging ratio [12]. Nevertheless, we remark that future in-depth investigations are needed to clarify this issue.

### 3.3. Manipulating air staging ratio to minimize $\text{NO}_x$ emission

Whether  $\text{NH}_3$  acts as the  $\text{NO}_x$  contributor or  $\text{NO}$  reductant heavily relies on the local atmosphere and the  $\text{NH}_3$  injection approach [8,9,12,14,29]. Thus, adjusting the air staging ratio can be a convenient way to change the local condition without physical modifications of the system. In this work, we adjust the solenoid valve controlling the secondary air flow rate and percentage during co-firing 30%-thermal  $\text{NH}_3$  with SH coal. Notice that the primary air valve is left unchanged. It leads to changes in the total flow rate and major gaseous emissions, as shown in Fig. 6. We see that by reducing the secondary air percentage from 64% to 16%,  $\text{NO}_x$  emission is remarkably mitigated from 2000 ppm to 300 ppm, while the excess  $\text{O}_2$  changes mildly (reduced from 8% to 4%).  $\text{SO}_2$  and  $\text{CO}$  increase from 300 to 500 ppm, and from 40 to 200 ppm, respectively. The reduction of  $\text{NO}_x$  emission may be primarily attributed to the lowered overall air ratios caused by the decreased secondary air ratio and a constant fuel supply. The less oxidizing environment, as indicated by elevated  $\text{CO}$  concentrations (see Fig. 6), suppresses the radical pool of  $\text{OH}$ ,  $\text{O}$ , etc., and weakens the intensity of  $\text{NO}_x$  formation through the fuel-N pathway [8,31]. Note that the  $\text{NO}_x$  emission of 300 ppm is even lower than pure SH coal combustion (without adjusting the air staging ratio). We need to mention that air staging manipulation has been proved effective for  $\text{NO}_x$  reduction in both pure ammonia combustion [12] and ammonia/nature gas co-combustion [32].

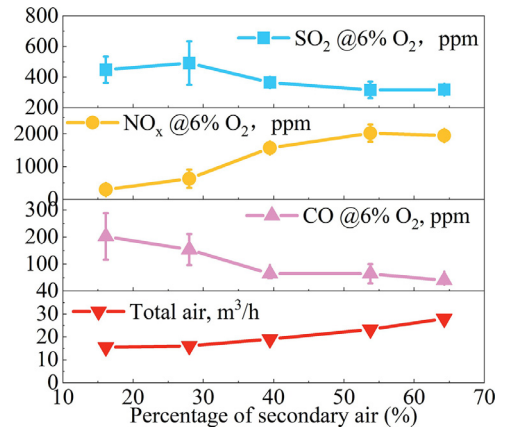


Fig. 6.  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{CO}$  emission and total air flow rate v.s. secondary air percentage in co-firing 30%-thermal  $\text{NH}_3$  with SH coal.

It implies a powerful way for existing coal units to partially burn  $\text{NH}_3$  even with non-optimized physical/structural retrofit.

### 3.4. Ash deposition

As for the ash-related issue, Fig. 7a illustrates the time evolution (within 1 h) of deposited mass onto the probe. Fig. 7b presents the visual morphologies of the ash deposits. Pure SH coal combustion generates deposits linearly growing with time from 0.22 g at 15 min to 0.77 g at 1 h. By contrast, adding 30%-thermal  $\text{NH}_3$  dramatically reduces the deposited mass to 0.45 g at 1 h. When the biomass CS is involved, remarkably more deposits have been collected on the probe than in the SH and SH- $\text{NH}_3$  combustion cases, indicating the enhancing effect of biomass on ash deposition. Meanwhile, except for pure SH, the deposits are collected more slowly at the time interval of 30–60 min than at the 0–30 min period. It could be attributed to the deposit shedding [22]. Stratified deposited layers are observed in Fig. 7b, with a light-colored fine inner layer covering the entire probe and the gray bulk deposits located on the windward side. At larger elapsed times, the ash deposits gain ‘rougher’ surfaces, implying more frequent ‘local shedding’ especially for the blend (SH: CS=4:1 without  $\text{NH}_3$ ). When mixing CS with SH, the contents of K and Na in the ash increase, including K from 2.06% to 3.67% and Na from 1.73% to 1.87% (see Table 1). As a result, bulk ash particles become stickier with the formation of AAEM-rich “coating layers” so that they are more prone to stay after impacting the probe [22,33]. The difference in the one-hour deposited masses between  $\text{NH}_3$ -addition and no- $\text{NH}_3$  cases is caused by the varying extents of shedding [34].

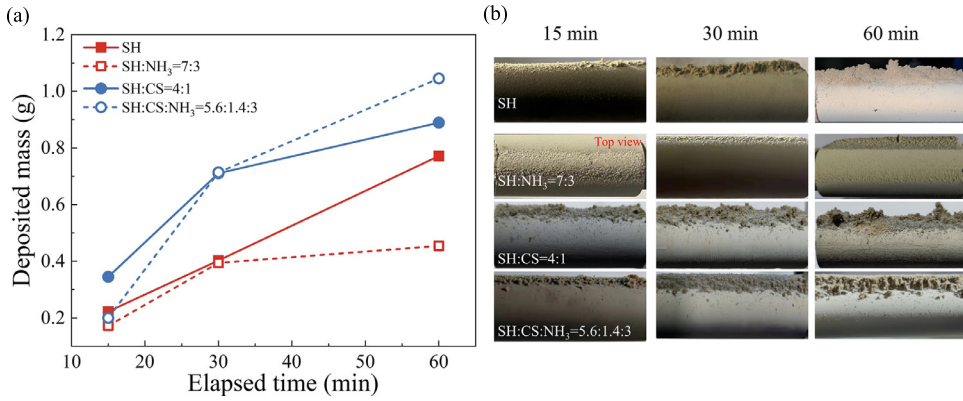


Fig. 7. (a) Time evolution of the deposited mass with elapsed time; (b) Visual morphologies of the deposits.

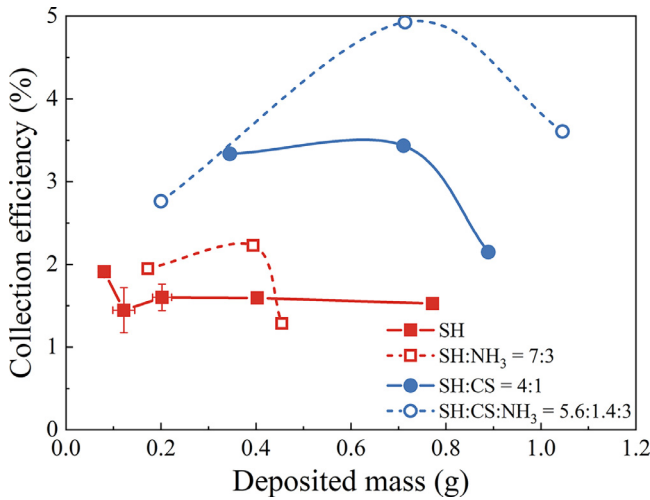


Fig. 8. Collection efficiency as a function deposited mass.

Fig. 8 further shows the normalized ash collection efficiency as a function of the deposited mass. The collection efficiency is defined as the fraction of deposited particles over the total incoming ash onto the projected area of the probe, formulated as  $CE(\%) = \dot{m}_d A_c / (\dot{m}_F Y_{ash} A_p)$ . Here  $\dot{m}_d$  is the ash deposition rate (kg/s) calculated by the ash deposited mass in a certain elapsed time,  $A_c$  is the cross-section area of the furnace (m<sup>2</sup>),  $\dot{m}_F$  is the fuel feed rate (kg/s),  $Y_{ash}$  is the ash content in fuels, and  $A_p$  is the projected surface area of the sampling probe (m<sup>2</sup>) [22,33]. It is a good indicator of the ash deposition propensity. For pure SH coal, the collection efficiency is  $\sim 1.5\%$ , a rather small value. Adding 30%-thermal NH<sub>3</sub> leads to small changes that could be explained by the shedding effect (the less coal/ash loading, the less propensity to shed). By contrast, the collection efficiency of co-firing with biomass CS tops 5%, a large value for coals with strong fouling propensities [22]. The contri-

butions of Na and K (with higher contents in the blended fuel, see Table 1) can be reasonably inferred [22,33].

### 3.5. Particle size distribution of fly ash in the coal burnout regime

Fig. 9a shows the particle size distributions (PSD) of particulate matter (PM) at P4 (the burnout regime) on the basis of unit input ash (mg/g<sub>ash</sub>), and Fig. 9b reports the yields of PM<sub>0.26</sub>, PM<sub>1</sub>, PM<sub>2.5</sub> and PM<sub>2.5-10</sub>. We merge the ELPI and APS data in Fig. 9a by converting the number PSDs from APS to the mass PSDs after simply assuming a uniform particle density of 2000 kg/m<sup>3</sup> [35]. We find that a reasonable agreement can be achieved between APS and ELPI+ (or DLPI+) measurements in the overlapping size range (0.5–10 μm) for burning pure SH coal and the SH–NH<sub>3</sub> (30%-thermal) blend. The overall



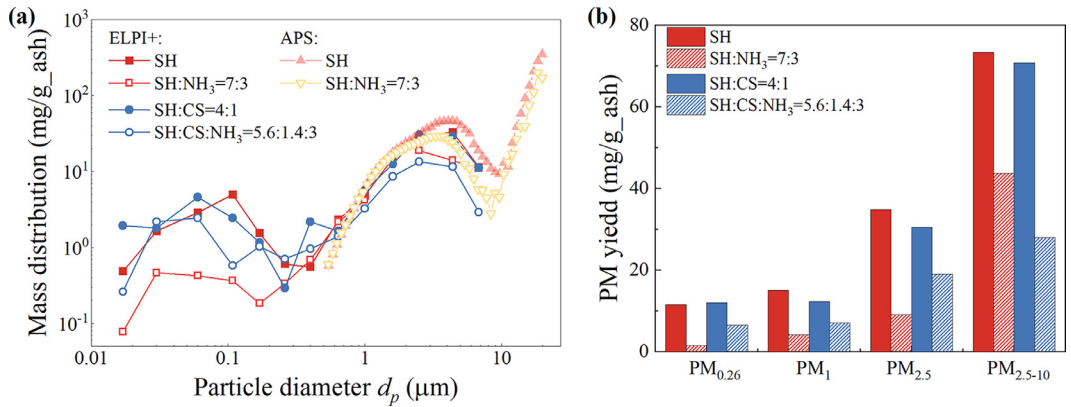


Fig. 9. (a) Particle size distribution ( $\text{mg/g}_{\text{ash}}$ ) and (b) PM yield ( $\text{mg/g}_{\text{ash}}$ ) of fly ash sampled at P4 for burning SH coal, SH-30% (thermal) NH<sub>3</sub> blend, SH-CS blend, and SH-CS-NH<sub>3</sub> blend. The number PSDs from 0.5 to 20  $\mu\text{m}$  measured by APS is converted to mass PSDs by assuming a constant density of 2000  $\text{kg/m}^3$ .

mass PSD from solid fuel combustion, even with NH<sub>3</sub> addition, is trimodal: (i) an ultrafine mode finer than 0.1  $\mu\text{m}$ , (ii) a micrometer mode peaked between 1 and 10  $\mu\text{m}$ , and (iii) a coarse mode with the peak size greater than 10  $\mu\text{m}$  (even beyond 20  $\mu\text{m}$ , the detection limit of APS) [36]. Generally, the ultrafine mode is formed by the pathway of nucleation-condensation-coagulation of vaporized minerals, the micrometer mode is mainly formed by the discrete included/excluded minerals via coalescence, fragmentation, et al., and the coarse mode is attributed to the unburnt char and bulk excluded ash in coal [26,36]. A comparison among the fuel types in Fig. 9b helps reveal the influences of NH<sub>3</sub> and biomass blending. In the ultrafine size range, co-firing SH coal with 30%-thermal NH<sub>3</sub> generates less PM, especially PM<sub>0.26</sub>, which accounting for only  $\sim 10\%$  of that from SH coal combustion. This seems to be a direct consequence of the lowered temperature (see Fig. 3b) and thus a weakened strength of minerals vaporization-nucleation-condensation. On the contrary, the PM<sub>0.26</sub> formation ability of the blend (SH:CS=4:1) is greater than pure SH coal (for more than 50%). The more abundant ultrafine particles and the exacerbated fouling tendency indicate the adverse effects of biomass co-firing. The ash-related problems seem to be minor for co-firing ammonia; Instead, the combustion intensity (unburned carbon) and NO<sub>x</sub> issues are the central concerns.

#### 4. Conclusions

In this paper, we study the NO<sub>x</sub> emission, carbon burnout, and ash-related issues in co-firing NH<sub>3</sub> with coal and biomass in a 25-kW down-fired combustor. By using a conventional swirl burner with central injection of NH<sub>3</sub> (up to 30% thermal

input), a complete burnout of NH<sub>3</sub> is achieved with only a trace amount of NH<sub>3</sub> slip detected.

While CO<sub>2</sub> and SO<sub>2</sub> concentrations decline linearly with the NH<sub>3</sub> fuel ratio, the NO<sub>x</sub> emission increases instead. Manipulating the air staging ratio by reducing the secondary air percentage is shown effective to reduce NO<sub>x</sub> down to  $\sim 300$  ppm.

For carbon burnout, we show a complex effect of NH<sub>3</sub> addition by increasing the unburnt carbon in fly ashes of coal-NH<sub>3</sub> mixtures while reducing it in cases co-firing coal, biomass and NH<sub>3</sub>. The possible mechanisms are discussed.

Co-firing NH<sub>3</sub> with either lignite coal or the coal-biomass blend reduces both the fouling intensity and the ultrafine particulate matter yield, as compared with the opposite influences of biomass co-firing. The observed trends seem to be consistent with the reduced coal feed rate and the temperature variations after NH<sub>3</sub> addition to the furnace.

Our work verifies the feasibility of co-firing NH<sub>3</sub> in existing coal units. Future work should be directed towards more detailed investigations of the air staging strategy and carbon burnout issues.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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