Contents lists available at ScienceDirect

Fuel

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Co-firing characteristics and fuel-N transformation of ammonia/pulverized coal binary fuel

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ARTICLE INFO

Keywords:

Ammonia

Co-firing

Carbon neutral

Emission reduction

Coal

ABSTRACT

As a feasible way to decarbonize coal combustion under the background of carbon neutrality in recent years, ammonia co-firing with pulverized coal is receiving considerable critical attention from the academic and industrial communities. This paper investigates the effects of coal type, NH₃ injection mode, temperature, excess air ratio (α) and NH₃ co-firing ratio (E_{NH3}) on combustion characteristics and fuel-N transformation of ammonia/ pulverized coal in a 6 kW drop tube furnace. Emission of O2, CO2, CO, NO, NO2 and NH3 at the furnace exit was monitored online. The unburned carbon (UBC) content and elementary composition in fly ash were also tested. Results show that NO_x generation behaviors of premixed and staged modes are significantly different. Typically, NO_x emission peaks at $E_{NH3} = 20$ % under high temperature and staged mode. As for NH_3 /coal cases at 1000 °C, NO_x level is even lower than pure coal combustion, but NH_3 residue is higher. The water gas shift reaction (WGSR) under fuel-rich condition generates more CO, and the conversion ratio from fuel-N to NO_x decreases when α diminishes. Ammonia co-firing can achieve lower CO emission with anthracitic coal from Gongyi (GYcoal) while lower NO_x emission with bituminous coal from Inner Mongolia (IM-coal). Ammonia co-firing can considerably improve the transformation from fuel-N to N₂. From the perspective of emission control and decarbonization, $E_{NH3} = 40$ % is an optimal ammonia co-firing ratio which not only can reduce half of CO₂ but also brings the conversion ratio from fuel-N to NOx and residual NH3 to the minimum level. The micromorphology of ash samples is greatly affected by coal/ammonia co-firing. In premixed mode, the surface of ash sample is porous and adhered to each other; while in staged mode, obvious fractures and cuts exist between the ash particles due to the sharp decrease of local gas temperature.

1. Introduction

Reduction of CO_2 emission is an urgent issue worldwide, and realization of a carbon-neutral society is widely discussed in recent years. The pressure for decarbonization is becoming stronger than ever before in every field especially for energy sector. How to achieve carbon neutrality while remaining cost-efficiency for existing thermal power stations has become a major challenge. It is a feasible strategy to partially replace coal by low carbon or carbon-free fuels reducing the carbon emission step by step. According to recent researches, ammonia is a promising solution as substantial fuel for coal. As a hydrogen-rich carbon-free fuel, ammonia has the advantages of high energy density, low cost, and safety for storage & transportation. In addition to the Haber-Bosch process, green ammonia can also be produced using renewable energy from wind or solar photovoltaic systems to power the ammonia synthesis process. Being an efficient method to directly reduce $\rm CO_2$ emission from source, ammonia co-firing with pulverized coal is receiving considerable critical attention from academic and industrial communities. For instance, as the world's first demonstration project with large amount of ammonia co-fired in large-scale commercial coal-fired power plant, JERA's Hekinan Thermal Power Station plans to conduct 20 % ammonia co-firing at 1000 MWe unit in Japan by 2024 [1].

Studies over the past several years have reported some progress of NH₃ co-firing technology. Aiming at problems of low combustion efficiency, flame instability and high NO_x emission of ammonia combustion, IHI Corporation has conducted numerical simulation studies[2–4] of coal/ammonia co-firing based on a commercial boiler. Zhang et al.[2] investigated the effect of NH₃ co-firing rate on the combustion characteristics and NO emissions. Results indicate significant influence of NH₃ co-firing rate to the flame shape. The outlet NO level decreases monotonically due to the DeNO_x effect when NH₃ co-firing rate >10 %. Once

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https://doi.org/10.1016/j.fuel.2022.126857

Received 19 September 2022; Received in revised form 10 November 2022; Accepted 20 November 2022 Available online 28 November 2022 0016-2361/© 2022 Elsevier Ltd. All rights reserved.



Full Length Article





NH₃ co-firing rate exceeds 40 %, the internal recirculation zone is completely penetrated by high velocity NH₃ flow, which leads to a long flame and much unreacted NH₃ leakage to downstream. Ishihara got similar results[3] and ascribed it to the NH₃ chemistry in rich and low temperatures ammonia flames. Moreover, Ishihara et al. [4] studied the effect of varied injection positions of NH₃ and obtained lower NO emission than the coal-fired case when NH₃ injected into flame zone in burner zone. Ma et al. [5] investigated the NH₃/coal co-firing characteristics and NO formation behavior in a 20 kW drop tube furnace by numerical calculation. They suggested the stoichiometric ratio be approximately 0.96 and inject ammonia as close as possible to the coal combustion flame zone.

In terms of experimental studies, Yamamoto et al.[6] explored the NO_x emissions of different ammonia side wall injection locations on through a 760 kW horizontal furnace. Takuma et al.[7] evaluated the characteristics of NH₃/coal co-firing with three ammonia injection methods using an 1.2 MW coal-fired furnace. The results indicated the injection of ammonia from the side walls will increase NO_x even for low co-firing ratios, and similar NO_x emission level of ammonia co-firing can be achieved as pure coal by adopting proper gas injection.

Although a few works have been conducted on ammonia/coal cofiring, divergences of emission characteristics and NO_x levels exist in literatures due to different burner structures, air-staged conditions, etc. Most of related studies have only carried out numerical simulations [2–5]. Apart from these modeling results, there is a general lack of systematic experimental research on pulverized coal co-fired with ammonia with various impact factors, especially the mixing type of ammonia and optimal NH₃ co-firing rate, which is essential for validation. Moreover, the DeNO_x effect of ammonia/coal co-firing process is not entirely understood. At the same time, there is little quantitative analysis of fuel-N transformation aiming for ammonia co-firing subject, which is very important for the understanding of NO_x formation and reduction.

In the field of ammonia direct combustion, further basic experiments needed to be carried out for revealing the concerted reaction mechanism of ammonia/coal co-firing process. Our previous study[8] obtained the co-firing characteristics of ammonia/coal basically at 1000 °C with 20 % NH3 blended. As for this work, we conduct the co-firing tests with different coal types and broaden the NH₃ co-firing ratio region (0–100 %) as well as the temperature interval (1000–1400 °C). This study can be said to be the first attempt of fuel-N transformation of ammonia/coal co-firing in high temperature furnace. One purpose of this work is to find out the optimal operating condition by measuring the emissions of exhaust gas help for the further engineering design. Generally, this paper will investigate the effects of coal type, ammonia co-firing mode, reaction temperature, total excess air ratio and ammonia co-firing ratio on combustion characteristics in a 6 kW staged drop tube furnace. In addition, unburnt carbon contents and compositions of fly ash with various ammonia/coal combustion cases were compared to explore the burning properties and fuel-N transformation mechanisms.

2. Experimental and methodologies

2.1. Experimental setup

As shown in Fig. 1(a), the experimental facilities for ammonia/coal co-firing test consists of a gas supply system, a loss-in-weight doublescrew micro-feeder (KTRON, USA), an air-staged electric heating drop tube furnace (LENTON, UK) and an online gas analyzer (Testo 350, Germany). A vertical corundum tubular reactor was housed inside the furnace with an inner diameter of 75 mm and a length of 2000 mm. The parallel electric heating components were controlled by 3216CC temperature program module to achieve uniform radiant heating inside the tubular reactor. The pulverized coal was introduced directly into the hot reaction zone assisted with primary air through a jet nozzle (inner diameter of 10 mm) at the top of the furnace. As for the injection method



Fig. 1. Schematic diagrams of (a) the NH_3 /coal co-firing experimental apparatus and (b) the sectional view of the drop tube furnace.

of ammonia, this work adopted two co-firing modes: premix and staged mode. For premix mode, ammonia was injected into the central pipe mixing with primary air i.e., pulverized coal and air stream. For staged mode, ammonia was blended with staged air and then injected down-stream of the burner through a staged pipe (inner diameter of 6 mm) with exit located 250 mm below the central nozzle. The bottom of the staged air inlet is sealed and the outlet hole faces the furnace axis, which can help the mixing of staged airflow and flue gas. The detailed cross-sectional structure of the drop tube furnace can be found in Fig. 1(b).

The air tightness of the combustion system can be decisive for the stability of reaction atmosphere. It is necessary to ensure the uniform temperature distribution and a sufficient particle heating rate in the furnace. Thus, before the experiments, the temperature distribution of furnace was calibrated by an S-type thermocouple which was inserted into the central pipe from top to bottom along the center line. The calibration curve (Fig. S1) showed that the thermal insulation performance of this furnace body was satisfactory, the temperature profile was quite stable and uniform, and the isothermal reaction zone was around 400 mm. Evaluated from gas flow rate and temperature under various experimental conditions, the residence time inside the furnace ranges from 3.1 to 6.2 s.

The coal feeding rate was controlled and monitored by the K-TRON micro-feeder with uncertainty of ~5%, which enabled to keep a precise and stable feeding rate down to 20 g/h. Since pulverized coal properties (e.g., coal type, particle size, moisture content) could directly influence the feeding rate, the air-dried coal supply rate was calibrated before each test. The calibration results (Fig. S2) showed that the feeding rates were highly linear with time, the fitting coefficients can reach $R^2 > 0.999$, indicating its stable coal supply ability.

The gas used in this work was provided by cylinder gas and precisely controlled by mass flow controllers (MFC, Alicat), among which the $\rm NH_3$ gas was controlled by a corrosion-resistant MFC.

2.2. Gas analysis and ammonia slip measurement method

The concentration of flue gas components at the furnace exit was continuously monitored by Testo 350 online gas analyzer. The final emission levels including CO₂/CO/NO/NO₂ were normalized to $6 \% O_2$ mole fraction as follows:

$$[M]_{6\%O_2} = [M]_{real} \cdot \left[(21 - 6) / (21 - [O_2]_{real}) \right]$$
⁽¹⁾

where $[M]_{6\%O_2}$ is the concentration of the flue gas component M cor-

rected by 6 % O_2 , $[M]_{real}$ is the measured concentration of M and $[O_2]_{real}$ is the measured mole fraction of O_2 in the flue gas.

For the ammonia slip downstream of the reaction zone for coal/ ammonia co-firing applications, ammonia leakage at exit of combustion facilities should be well controlled. According to the experience of thermal power plants in the USA[9], the ammonia slip at the exit of boiler mainly accumulates in fly ash at air preheater and dust collector. The actual ammonia level in the flue gas discharged from the chimney is generally quite low. Thus, the mass fraction of ammonia in fly ash can be used as indicator for ammonia slip[10]. The residual ammonia in fly ash was quantitatively measured by Nasser's reagent spectrophotometry in this study (Detection limit ~0.25 μ g NH⁺/10 ml). As for the gaseous ammonia slip of pure NH₃ cases, the flue gas was continuously injected into a gas collecting cylinder containing 50 ml of H₂SO₄ (0.1 mol/L) for 5 min at the flow rate of 1 L/min and then analyzed by the spectrophotometer. The final NH₃ concentration was converted into volume fraction (ppm). Here, the NO_x is sum of NO and NO₂.

2.3. Coal property and test conditions

This study investigates two kinds of typical coals including bituminous coal from Inner Mongolia of China (IM) and anthracitic coal from Gongyi of China (GY). The results of their proximate and ultimate analysis are shown in Table 1. Before each test, the samples were first air-dried for 6 h at 105 °C and sieved to the particle size below 300 μ m.

Detailed operational conditions of the present pulverized coal/ ammonia co-firing experiment are summarized in Table 2. In this study, the major parameters are as follows:i) coal type: IM/GY;ii) reaction temperature: 1000/1200/1400 °C;iii) total excess air ratio α : 1.2/1.0/ 0.8;iv) ammonia injection method: Premix mode/Staged mode;v) ammonia co-firing ratio $E_{\rm NH3}$: 0/10/20/40/60/100 %. It should be noted that: in the premix mode, coal/NH₃/air were all pass through the central pipe and injected into the furnace at the central nozzle; while in the staged mode, coal/primary air pass through the central pipe and NH₃/secondary air were injected into the downstream of the furnace through the staged pipe outlet at 250 mm below the central nozzle. The ammonia co-firing ratio $E_{\rm NH3}$ is defined in terms of heating value in the mixed fuel as:

$$E_{NH_3} = \frac{q_{NH_3} \times \rho_{NH_3} \times Q_{NH_3}}{q_{coal} \times FR}$$
(2)

where q_{NH3} and q_{coal} are the heating value of NH₃ and coal, respectively, in J/g; ρ_{NH3} is the density of NH₃, in g/L; Q_{NH3} is the flow rates of NH₃, in L/min; *FR* is the coal supply rate, in g/min.

2.4. Fuel-N transformation definition

To quantify the transformation of nitrogen in the coal/ammonia cofiring process, the specific transformation paths of fuel-N were investigated. According to the operational conditions of this study, considering the resident time of pulverized coal in the furnace (3.1-6.2 s) and the reaction temperature, the conversion ratio of tar could be neglected (<0.1 %). Meanwhile, assuming that there is no ash loss throughout the whole combustion process, the fuel-N conversion ratios can be calculated according to the conservation of ash. The fuel-N conversion ratios involved in this paper are defined as follows:

Table 2

Testing conditions of the co-firing experiments.

Operation parameters	Unit	IM-coal	GY-coal
Thermal input	W	305	332
Coal supply rate (FR)	g/h	40/36/32/24/16/0	40/32/24/16/0
Ammonia flow rate	L/	0-1.274	0-1.389
(Q_{NH_3})	min		
Ammonia co-firing ratio	%	0/10/20/40/60/100	0/20/40/60/100
(E_{NH_3})			
Ammonia co-firing	-	Premix mode/Staged	Premix mode/Staged
methods		mode	mode
Staged air ratio of total air	%	30	30
Total excess air ratio (a)	_	0 8/1 0/1 2	12
Reaction temperature	°C	1000/1200/1400	1000/1200/1400

$$CR_{NO_x} = \frac{[NO_x] \times Q_{total} \times M_N}{10^6 \times (V_M \times FR \times N_{ad\ coal}/100 + Q_{NH_3} \times M_N)} \times 100\%$$
(3)

$$CR_{NH_3} = \frac{[NH_3] \times Q_{total} \times M_N}{10^6 \times (V_M \times FR \times N_{ad,coal}/100 + Q_{NH_3} \times M_N)} \times 100\%$$
(4)

$$CR_{Ash_N} = \frac{N_{ad,Ash} \times FR \times Ash_{ad,coal} / Ash_{ad,Ash}}{FR \times N_{ad,coal} + Q_{NH_3} \times M_N / V_M} \times 100\%$$
(5)

$$CR_{N_2} = 1 - (CR_{NO_x} + CR_{NH_3} + CR_{Ash_N})/100$$
(6)

where CR_{NO_x} , CR_{NH_3} , CR_{Ash_N} and CR_{N_2} are the conversion ratios of fuel-N to NO_x, NH₃, Ash-N and N₂, respectively; $[NO_x]$ is the concentration of NO_x in the flue gas sampled at the furnace exit, in ppm; M_N is the molecular weight of N atom, namely 14 g/mol; V_M is the molar volume of gases under STP, namely 22.4 L/mol; *FR* is the coal supply rate of experimental cases, in g/min; Q_{total} and Q_{NH_3} are the flow rates of total flue gas and NH₃ under STP, respectively, in L/min; $N_{ad,coal}$ and $N_{ad,Ash}$ are the nitrogen contents of raw coal and ash, respectively, on air-dried basis, in wt%; $Ash_{ad,coal}$ and $Ash_{ad,Ash}$ are the ash contents of raw coal and ash, respectively, on air-dried basis, in wt%.

3. Results and discussion

3.1. Emission characteristics for different co-firing conditions

3.1.1. Effect of ammonia co-firing methods on emission characteristics

Fig. 2 shows the flue gas compositions and unburnt carbon (UBC) content at the furnace exit with $E_{\rm NH3}$ increases from 0 to 60 % for both premix/staged modes at 1200 °C and $\alpha = 1.2$. The columns from left to right represent the NO_x/CO/CO₂ concentrations and the UBC contents of pure coal, premix co-firing mode and staged co-firing mode, respectively. The concentrations of flue gas compositions are normalized to 6 % O₂. The unburnt carbon (UBC) content is defined as the proportion of the unburnt carbon in the final flying ash to the raw coal, which is calculated according to the ash balance as follows:

$$UBC = C_{ad,Ash} \times Ash_{ad,coal} / Ash_{ad,Ash} \times 100\%$$
⁽⁷⁾

where $C_{ad,Ash}$ is the carbon content of fly ash on air-dried basis, in wt%. As can be seen in Fig. 2, the CO₂ content of the flue gas under both premix mode and staged mode decreased proportionally with the

Table 1

Proximate a	and	ultimate	analysis	of the	coal	sample.	

Coal	Proximate analysis (wt %)			Q _{net,ad} (MJ/kg)	Ultimate analysis (wt %)					
	M _{ad}	A _{ad}	V _{ad}	FC _{ad}		C _{ad}	H _{ad}	N _{ad}	S _{t,ad}	O _{ad}
IM	3.68	8.64	30.76	56.92	27.41	68.58	4.57	0.88	0.43	13.22
GY	2.86	11.50	10.67	74.97	29.87	78.96	3.22	1.30	0.29	1.87

Note: ad, on air-dried basis; M, moisture content; A, ash content; V, volatile content; FC, fixed carbon; Q_{net}, low heating value; S_t, total Sulphur.



Fig. 2. The effects of ammonia co-firing methods on the emission performances of the flue gas compositions and UBC contents (IM-coal, 1200 °C, $\alpha = 1.2$).

increase of E_{NH3} . Comparing with pure coal combustion, the decarbonization rate at $E_{NH3} = 40$ % could reach 47.13 % and 54.30 %, respectively. The main oxidation reactions of NH₃ during co-firing process include[11]:

 $2NH_3 + 3/2O_2 \rightarrow N_2 + 3H_2O$ (R1)

$$2NH_3 + 5/2O_2 \rightarrow 2NO + 3H_2O \tag{R2}$$

$$2NH_3 + 7/2O_2 \rightarrow 2NO_2 + 3H_2O \tag{R3}$$

Since the decarbonization strategy of partially substitution of coal by ammonia would directly introduce extra fuel-N, it is necessary to focus on the emission characteristics of *N*-containing components during the coal/ammonia co-firing process. Red columns in Fig. 2 indicate evident increases of NO_x emission at co-firing cases compared with the pure coal case, but still on the same magnitude.

The NO_x formation performances of two co-firing modes were distinctly different. This may be due to the delayed mixing process of fuels and oxidizer for staged mode, which led to incomplete combustion of pulverized coal at the main combustion region. Also, the local reducing atmosphere at the staged tube outlet (with overall NH₃ and 30 % of total air) would influence the formation of fuel-NO_x in ammonia flame and the selective non-catalytic reduction (SNCR) reactions between NO_x and NH₃. Detailed mechanisms are further discussed below.

Regarding to the UBC contents, both premix and staged modes showed an overall increase with $E_{\rm NH3}$, which indicated that $\rm NH_3$ addition inhibited the burnout of coal to a certain degree. This could be attributed to the heterogeneous ignition mechanism of coal/ammonia as follows. The ignition of $\rm NH_3$ flame quickly consumes the oxygen around the pulverized coal surface. At the same time, the thermal radiation effects from coke, fly ash and soot particles produced by coal combustion will suppress the flame temperature and thereby lead to lower burnout rates of coal particles at high $E_{\rm NH3}$. Thus, the combined effects between pulverized coal and ammonia caused the gradual increase of UBC with rising $E_{\rm NH3}$ in Fig. 2. As for the higher UBC contents of staged mode, it was due to the hesitance of coal burnout caused by delayed supply of O_2 , which led to longer flares and lower flame temperature.

3.1.2. Effect of reaction temperature on emission characteristics

Fig. 3 shows the flue gas compositions including CO₂/CO/NO_x and residual NH₃ in fly ash under various E_{NH3} (0–60 %) and different temperature conditions (1000/1200/1400 °C) for IM-coal co-fired with ammonia. The total excess air ratio α was set to 1.2 as constant. The

results on the left were measured in the premix mode while the ones on the right represented the staged mode.

The concentration of CO_2 showed a linear negative correlation with $E_{\rm NH3}$ for both premix and staged modes. As the reaction temperature went up, the CO_2 production increased consequently, indicating higher burnout rate under elevated temperature.

As for CO emission levels, the curves for both two modes decreased at first and then increased with rising $E_{\rm NH3}$. At low $E_{\rm NH3}$, apart from the reduction of coal supply, it can be speculated that with the enrichment of H_2O in the combustion region, the oxidation of CO can be improved through the major elemental reaction route of R4 with OH, consuming CO in the flue gas:

$$CO + OH \rightarrow CO_2 + H$$
 (R4)

The subsequent increasing trends might be due to the water-gas reaction R(5) between the abundant water vapor and the unburnt carbon at high E_{NH3} and high-heat atmospheres. In the meantime, gasification reaction R(6) would also occur between CO_2 and C in char under anoxic conditions to generate a handful of CO:

$$C + H_2 O \rightarrow CO + H_2 \tag{R5}$$

$$C + CO_2 \rightarrow 2CO$$
 (R6)

According to the studies related to denitration effect of coal-fired boilers by spraying ammonia[12,13], it was found that the more NH₃ injected, the higher CO concentration in the flue gas. The reduction process of NO_x by NH₃ would not generate CO, however, since the competitive effect of NH₃ molecules for active radicals e.g. O/OH, plenty of free radicals were consumed in the ignition stage where NH₃ decomposed rapidly. It is well-known that the reaction rate of CO oxidation process is fairly slow and dependent on active radical concentration such as OH. Therefore, the consumption of CO would be inhibited with the increase of E_{NH3} , which led to higher CO levels in the flue gas. Comparing to the NH₃ co-firing ratio or the equivalence ratio of fuel/oxidizer, the influences of temperature on the CO emission were less significant under the present conditions with constant α and coal supply rates.

Based on Fig. 3, there are significant differences between the NO_x emission characteristics of two ammonia co-firing modes. In the premix mode, the NO_x emission under moderate temperature (1000 °C) conditions increased slightly and then decreased monotonously with rising $E_{\rm NH3}$; and the NO_x emission under high temperature (1200 °C/1400 °C) conditions showed an overall rising trend and increased sharply at high $E_{\rm NH3}$. However, in the staged mode, the NO_x level went down monotonously at 1000 °C; and the curves showed a distinct peak near $E_{\rm NH3} = 20$ % and subsequently decreased to 2–3 times the NO_x level of the pure coal case.

Regardless of the ammonia co-firing mode and E_{NH3}, the NO_x emission levels at high temperature (1200°C/1400 °C) are much higher than that at moderate temperature (1000 $^\circ \text{C}$). This can be contributed to the dual effects of temperature on $\ensuremath{\text{NO}_x}$ generation: On the one hand, high temperature could promote the process of N-containing compounds in the coal and ammonia converting to NOx, but excessive temperature would exceed the SNCR reactions temperature window of NOx reduction. On the other hand, although the rising temperature facilitates the homogeneous/heterogeneous reduction reactions of NH₃/NO_x and coke/NO_x, it also accelerates the combustion process of NH₃ and coal. It should be noted that as temperature increased to 1400 °C, the NO_x concentration kept going up in the premix mode but slightly went down in the staged mode. Such phenomenon was also observed in the research of Sun et al.[14], which showed that temperature could have opposite effects on NO_x emissions in the flue gas under different atmosphere. Specifically speaking, the increasing temperature in reducing atmosphere would lead to a lower NO_x generation, while the opposite in oxidizing atmosphere. This conclusion corresponds to two co-firing modes in the present study: In the premix mode, the pulverized coal



Fig. 3. Effect of reaction temperature on emission characteristics. (IM-coal, $\alpha = 1.2$).

and NH₃ were mixed in the central pipe and fully combusted in the oxidizing atmosphere of primary air ($\alpha = 1.2$). However, in the staged mode, the pulverized coal in the flame upstream consumed part of O₂ in advance and then mixed with NH₃ and the secondary air at the outlet of the stage pipe, which created a locally anoxic atmosphere. Such principle is similar to the Rich Reagent Injection (RRI) technology which reduces NO_x formation by injecting amine-based compounds into the fuel-rich regions of furnaces. Two full-scale demonstrations on EPRImember utility units, Conectiv's 160 MW B. L. England Unit 1 and AmerenUE's 480 MW Sioux Unit 1 applied this NO_x control technology.

In the aspect of residual NH₃ content at the furnace exit, temperature assumed the decisive factor. The residual NH₃ in fly ash at 1000 °C behaved much higher than that of high temperature (1200°C/1400 °C). In the premix mode, the reaction temperature above 1200 °C could ensure that the residual NH₃ remain below 300 ppm of various ammonia

co-firing ratios, which is equivalent to 1/4 of the residual NH₃ at 1000 °C. However, in the staged mode, the NH₃ curves of high temperature cases got the maximum value near $E_{\rm NH3} = 40$ %, and the overall NH₃ levels were higher than that in the premix mode. This result can be attributed to the short residence time of NH₃ injected at the staged pipe outlet in the staged mode. In addition, in the cases of medium ratio of $E_{\rm NH3}$, a large amount of O₂ was consumed in the coal-fired region, which caused insufficient combustion of NH₃. Thus, the remaining unburnt NH₃ slipped at the exit of the furnace in the staged mode.

3.1.3. Effect of excess air ratio α on emission characteristics

Fig. 4 shows the flue gas compositions including CO₂/CO/NO_x and residual NH₃ in fly ash under various E_{NH3} (0–100 %) of different excess air ratios ($\alpha = 1.2/1.0/0.8$) for IM-coal co-fired with ammonia. All cases were conducted at 1200 °C.



Fig. 4. Effect of excess air ratio α on emission characteristics. (IM-coal, 1200 °C).

The concentration of CO₂ was highly linear with $E_{\rm NH3}$ for both two co-firing modes as expected. Also, the CO₂ emissions would decrease orderly as α declined from 1.2 to 0.8, which revealed the anoxic condition led to insufficient combustion of coal particles and lower burnout rates. During the experimental operation, denser smoke dust was indeed observed at the bottom chamber.

The CO emission levels of the two co-firing modes were similar at the fuel-lean sides ($\alpha=1.2$), but increased rapidly with the rising E_{NH3} when $\alpha\leq1$ in the staged mode.

Compared with the effects of temperature, α played a more crucial role in the generation of CO. Therefore, for the practical combustion facilities, sufficient air supply could ensure great CO reduction as well as considerable improvement of the overall combustion efficiency.

As for the NO_x emission characteristics, there was a significant difference between the two ammonia co-firing modes: The NO_x generated in the premix mode displayed exponential rising trends; Interestingly, the NO_x concentrations in the staged mode would reach the peak values near $E_{NH3} = 20$ % and then remain at a lower level below 1000 ppm. The divergence of the effect of temperature and α on the NO_x emission is that the NO_x generation curves under three sets of α behaved basically the same trends, while in different amplitudes of variation. To be more specific, the NO_x levels at $\alpha = 0.8$ were all lower than those at $\alpha = 1.2$, with discrepancies became larger as E_{NH3} increased. And that discrepancy of NO_x release between different α reached the maximum in the pure NH₃ case for both premix and staged modes. Kobayashi et al.[15] studied the effect of excess air ratio on NO_x generation in a one dimensional drop furnace under oxygen-enriched combustion conditions. They found that with the increase of α , the NO_x release increased first and then decreased, where the peak value occurred when $\Phi = 0.8$ (i. e. $\alpha = 1.25$). Such conclusion is completely consistent with the present

experimental results. Combined with the change rules of CO in Fig. 4(c) (d), it can be inferred that the increase of CO under the fuel-rich condition brings out more C(O) coordination compounds and free carbon active sites C_f generating on the particle surfaces through R7 and the heterogeneous reduction reaction R(8) between the char and NO_x :

$$2C(O) + 2NO \rightarrow N_2 + 2CO_2 + 2C_f \tag{R7}$$

$$2C + 2NO \rightarrow N_2 + 2CO \tag{R8}$$

promotes the NO reduction in the drop furnace and brings down the final NO_x levels of the co-firing process. It also verifies the reliability of the flue gas emission characteristics of coal/ammonia co-firing under various α of this section.

According to Fig. 4(e)(f), it can be seen that under the higher temperature close to the real combustion chamber, the ammonia injection modes have a decisive influence on the NO_x generations (E_{NH3, peak} = 100 % for premix mode and E_{NH3, peak} = 20 % for staged mode). Moreover, the NO_x levels decrease with the decline of α , which indicates the low emission of nitrogen oxides can be achieved by adjusting the excess air with constant thermal input power in the real combustion applications. It is worth noting that for both two co-firing modes, the NO_x generation of E_{NH3} = 40 % (range: 369.6–686.1 ppm under various α) could achieve similar levels to that of pure coal cases.

For the residual NH₃ in fly ash, the effects of α were significant as shown in Fig. 4(g and h), where the NH₃ residue under the fuel-lean ($\alpha =$ 1.2) conditions was generally lower than the stoichiometric ($\alpha = 1$) and fuel-rich ($\alpha = 0.8$) conditions. Particularly, the excess air in the cases of high E_{NH3} can guarantee a relatively low NH₃ level (<400 ppm) at the furnace exit. In the premix mode, the residual NH₃ showed the overall increasing trends with $E_{\mbox{\scriptsize NH3}}$ in the air-lean cases but there was a sink at $E_{\text{NH3}}=40$ %. By contrast, the residual NH_3 in the staged mode behaved the parabolic trends under different α . Specifically, the maximum NH₃ of the oxygen-rich cases was 571 ppm at $E_{NH3} = 40$ %, and the peak value of the residual NH3 increased to 1200 ppm under the stoichiometric and anoxic conditions at $E_{NH3} = 60$ %. However, even for the pure ammonia cases ($E_{NH3} = 100$ %), the NH₃ concentration at the exit could attain <150 ppm, which indicates that proper control strategies might be promising to reach the flue gas emission standards of the future NH₃ cofired combustors.

3.1.4. Effect of coal types on emission characteristics

To investigate the effect of different coal types, the pollutant (CO/NO_x) emission levels of IM-coal/GY-coal co-fired with ammonia under various $E_{\rm NH3}$ (0–60 %) were compared in Fig. 5. The reaction temperature was set to 1200 °C and the total excess air ratio α was set as 1.2.

Since GY-coal has fairly lower volatile content and higher fixed carbon content than IM-coal, the ignition temperature will be higher and the burnout rate will be lower under the same conditions. This is reflected in the measured flue gas contents of which the residual O_2

volume percentages for GY-coal were larger than IM-coal, and the measured CO_2 concentrations were opposite.

With respect to CO, the overall emission levels of GY-coal were much lower (<202.2 ppm) than those of IM-coal and showed decreasing trends with $E_{\rm NH3}$, and the drop ranges were larger in the staged mode as the CO concentration was approximately equal to 0 at $E_{\rm NH3} = 60$ %. It can be attributed to the rapid decomposition of NH₃ molecules as hydrogen carriers during the coal/ammonia co-firing, resulting in high content of H and OH radicals in the reaction zone. Moreover, the burnout of NH₃ brings more H₂O, which will promote the CO consuming reaction R(4).

Based on Fig. 5, the formation of $\rm NO_x$ in the premix mode for two coal types both increased exponentially with $\rm E_{\rm NH3}$, and reached the peak value when $\rm E_{\rm NH3}=60$ %. In the staged mode, however, the NO_x concentration would reach a relatively low level 417–686 ppm at $\rm E_{\rm NH3}=40$ % for both two coal types. It can be inferred that a considerable proportion of the fuel NH₃ as the reductant react with the nitrogen oxides (mainly NO) in such ammonia/coal mixing atmosphere through R9-R12:

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \tag{R9}$$

 $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (R10)

$$4NH_3 + 2NO + 2O_2 \rightarrow 3N_2 + 6H_2O$$
 (R11)

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$
 (R12)

The 1200 °C condition was close to the optimal temperature window (1120–1450 K) for Thermal DeNO_x which was proposed by Miller and Klippenstein[16]. There are many previous studies on the interactions of NH₃/NO[17–26], however, most of the experimental researches were conducted at the medium and low temperature region. Considering that the interactions of NH₃/NO occurs in the conditions over 1500 K in the flame of coal/ammonia co-firing process, it is urgent to study and reveal the mechanisms of NH₃ and NO at high temperature.

The non-monotonically trends of NO_x in Fig. 5(b) for both two coal types might be due to the change of dominant factors for NO_x generation under different NH₃ co-firing ratios in the staged combustion mode. The first decreasing trend resulted from the combined inhibiting effects of high local equivalence ratio on the fuel-NO_x generation and decreasing flame temperature on the thermal-NO_x. The rising trends of NO_x when $E_{\rm NH3} > 40$ % can be attributed to the increase of net fuel-NO_x generation with high NH₃ injection. Besides, the ultra-low coal supply under high $E_{\rm NH3}$ conditions caused the lack of char for NO reduction. Moreover, the abundant H₂O attached to the pulverized coal surfaces would further restrain the heterogeneous reduction process between gas/solid components. These factors together resulted in considerably high concentration of final NO_x emissions.

Comparing the results of the pollutant emission characteristics of IMcoal/GY-coal co-fired with NH_{3} , it can be inferred that NH_{3} co-firing



Fig. 5. Effect of coal types on emission characteristics. (1200 °C, $\alpha = 1.2$).

with GY-coal could obtain lower CO emission, while NH₃ co-firing with IM-coal could achieve lower NO_x emission. For the application of blending NH₃ in the industrial coal-fired boilers, it is recommended to select high volatile coal, and adopt the staged ammonia injection mode with 40 % NH₃ co-firing under moderate temperature to achieve ideal CO and NO_x emissions.

3.2. Fuel-N transformation during ammonia/pulverized coal co-firing processes

3.2.1. Effect of reaction temperature on fuel-N transformation

Fig. 6 depicts the conversion rates of 3 types of nitrogen occurrence forms and unburnt carbon rate in fly ash for IM-coal co-fired with 40 % NH₃. The total excess air ratio was controlled at $\alpha = 1.2$. Since the reaction temperatures of this study were all lower than 1500 °C, the oxidation conditions from N₂ to thermal-NO through the Zeldovich mechanism have not been reached. Combined with the little variation of NO_x emission for pure coal cases under different temperatures in Fig. 3, it can be concluded that the thermal-NO_x and prompt NO_x formation effect can be neglected in this section, which means the NO_x conversion rates under various temperature (1000/1200/1400 °C) could represent the fuel nitrogen (fuel-N) conversion from ammonia/coal to fuel-NO_x.

The combustion process of pure coal includes homogenous combustion of volatile components and heterogenous combustion of char. For the coal/ammonia co-firing process in this study, it should also consider the homogenous combustion of ammonia and the heterogenous reactions of ammonia/char. Therefore, nitrogen in coal and ammonia will transform into the gas phase or remain in fly ash as various *N*containing products in such process. Different from the traditional coal combustion, the fuel-NO_x sources of coal/ammonia co-firing include NO_x generated from *N*-element in volatiles, char and ammonia.

It is worth noting that the fuel-N mentioned above includes N elements of coal as well as NH_3 . The detailed definition formula of the conversion rate for each *N*-containing component has been listed in section 2.2.

It can be easily inferred from Fig. 6 that nitrogen migration distribution ranks of coal +40 % NH₃ cases: $CR_N_2 > CR_Ash-N > CR_NO_x > CR_NH_3$. Specifically speaking, most of fuel-N in the coal/ammonia cofiring process converted into complete combustion product N₂ (\geq 97.82 %). Among the rest fuel-N transforming paths, the Ash-N could reach the minimum level (0.76 %) at 1400 °C, which is approximately the same as CR_NO_x, but still higher than the proportion of residual NH₃ in flue gas and fly ash. In addition, the variation trends of Ash-N behave highly consistent with the UBC lines, which indicates the changes of the burnout rate due to different temperatures would reflect in the Ash-N content.

Both two NH₃ injection modes showed larger CR_NO_x at high



Fig. 6. Fuel-N conversion distribution of different reaction temperature (E $_{\rm NH3}$ = 40 %).

temperature than medium temperature conditions. CR_NO_x could attain 0.95 % and 0.74 % at 1400 °C for premix mode and staged mode, respectively, which increase several times comparing to CR_NO_x (0.21 % and 0.09 %) at 1000 °C. Combined with the dropping trends of Ash-N, it can be speculated that the rising temperature promoted the conversion of *N*-containing components to NO_x in the co-firing process, and the nitrogen remained in fly ash is more likely oxidized to NO.

With the increase of reaction temperature, CR_NH_3 showed an obvious monotonous decreasing trend which is opposite to the increasing trend of CR_NO_x . This can be attributed to the enhanced chemical reaction of ammonia. In the meantime, the residual NH_3 at the burner exit is significantly reduced and CR_NH_3 reaches only 0.02 % at 1400 °C.

3.2.2. Effect of excess air ratio α on fuel-N transformation

Fig. 7 shows the conversion rates of three types of nitrogen occurrence forms and UBC contents with various α for IM-coal + 40 % NH₃ at 1200 °C. Although the major NO_x production of pulverized coal combustion is fuel-type NO_x, the volatiles pyrolyzed and form active CH_i radicals under high temperature and fuel-rich conditions ($\alpha < 1$), which would generate prompt-NO_x on the diffusion flame surface. The Fenimore mechanism^[27] indicated that the prompt-NO_v is irrelevant to temperature, but highly dependent on the excess air coefficient α . In addition, literatures about the NOx emission in NH3 flame[28,29] reported significant divergences of NO generation in NH₃ combustion at different equivalence ratios. Therefore, this work studied the fuel-N transformation paths of different excess air ratio α in the coal/ ammonia co-firing process. The results show that with the decrease of α , namely when changing from lean side to rich side, the change of CR Ash-N and CR_NH₃ are not statistically significant, while the CR_NO_x shows a monotonous decreasing trend.

Specifically, CR_NO_x for premix mode decreases from 0.48 % to 0.30 % when α changes from 1.2 to 0.8, while for staged mode it decreases from 0.80 % to 0.36 % in the same situation. The main reasons are listed as follows: Firstly, in the fuel-rich conditions, the instantaneous-NO_x generated from the Fenimore mechanism would react with the hydrocarbons and intermediates i.e. HCN through the pyrolysis of coal volatiles in the reducing atmosphere. Secondly, the vital NNH mechanism of NH₃ combustion is inhibited under anoxic conditions when $\alpha < 1$:

$$N_2 + H \rightarrow NNH$$
 (R13)

$$NNH + O \rightarrow NO + NH$$
 (R14)

As a validation, the PLIF study of pure NH_3 combustion by C. Brackmann et al.[30,31] indicated a higher relative abundance of NH_i radicals for fuel-rich NH_3 flames. Thirdly, the incomplete combustion of pulverized coal results in an increase of CO concentration as shown in Fig. 4(c and d), and then a part of NO will be reduced under the catalytic



Fig. 7. Fuel-N conversion distribution of different α (E $_{\rm NH3}=$ 40 %).

action of char. These three combined effects lead to the gradual decrease of CR_NO_x with the dropping α for the coal/ammonia co-firing cases in this work.

3.2.3. Effect of NH₃ blending ratio E_{NH3} on fuel-N transformation

During the coal/ammonia co-firing process, there exists a significant difference in the fuel-N transformation characteristics due to the divergences in ammonia blending ratios and injection modes. Fig. 8 plots the percentages of fuel-N conversion paths for the IM-coal co-fired with various $E_{\rm NH3}$ at 1200 °C and $\alpha = 1.2$ under premix/staged mode.

It can be seen from Fig. 8 that in the pure coal cases, the percentages of CR_Ash-N are quite high up to nearly 50 % and the proportion of CR_NO_x could also reach nearly 20 %. With the increase of E_{NH3} , the proportion of fuel-N converted to Ash-N and NOx decreased significantly in both premix and staged modes. And the large CR N₂ value indicates that with NH₃ injection, most of the fuel-N of pulverized coal and NH₃ transformed into N2. Such a conclusion can verify that the coal/ ammonia co-firing strategy will effectively improve the conversion rate of overall nitrogen migrating to N₂, as well as reduce the proportion of fuel-N to Ash-N and harmful N-containing gas pollutants. This is mainly due to two aspects: on the one hand, NH₃ replaces part of coal with equaling heat values, while the nitrogen content of NH₃ (82.4 %) is much higher than that of coal (\sim 1%). Therefore, the increase of total nitrogen in fuel and the decrease of ash production led to a sharp reduction in the proportion of Ash-N. On the other hand, through the gasification reaction between the coal particles and the vapor generated by NH₃ combustion, some N-containing heterocycles in the ash are broken up, which accelerates the precipitation of N-element and converts into gas phase components, resulting in the decrease of CR_Ash-N. It is worth noting that the $\ensuremath{\text{NO}_x}$ conversion rate in the staged mode is much higher than that in the premix mode when $E_{NH3} = 20$ %, which might have a certain guiding significance for coal/ammonia co-firing applications with low NH3 blending ratios. On the whole, the percentage of fuel-N converted into residual NH3 is extremely low which is nearly indistinguishable in the distribution bars of Fig. 8. This is undoubtedly an advantage for the safe and clean utilization of ammoniafuel.

3.2.4. Effect of coal types on fuel-N transformation

Fig. 9 plots the conversion ratios of NO_x and NH₃ of the two types of pulverized coal (IM-coal/GY-coal) tested in this study with various $E_{\rm NH3}$ at 1200 °C. Apparently, the conversion ratios of *N*-containing pollutants of pure coal and pure NH₃ combustion are both higher than coal/ammonia co-firing cases. It could be attributed to the heterogenous



Fig. 8. Overall fuel-N transformation distribution with various E_{NH3}.



Fig. 9. Conversion ratios of NO/NH₃ for IM/GY-coal (1200°C, $\alpha = 1.2$).

NH₃/char reactions and the differences in the denitrification effect of these two types of coal might be reverent to the reactivity of char.

Compared with IM-coal, GY-coal has lower CR NO_x values especially in premix mode. And the levels of CR NH3 are relatively close, while GYcoal is slightly higher for pure coal case. Literatures about the migration of fuel-N during the combustion process of different coal types could verify such conclusion. For instance, Chen[32] and Huang[33] studied the NOx release behaviors of coal combustion in the O2/CO2 atmosphere on the drop tube furnace and stationary bed respectively. They found the conversion ratio of fuel-N to NO_x of high-rank coal is higher than that of low-rank coal, which is consistent with the CR_NOx results of IM/GYcoal in Fig. 9. It can be explained that because of different coal ranks, the volatile content of IM-coal is >3 times that of GY-coal. As a result, the gas phase components such as HCN and NH₃ released by coal pyrolysis will participate in the high temperature oxidation located in the main reaction zone where the volatiles are quickly burned out and converted into more fuel-NO. In addition to temperature, the environment near the particles is more fuel rich for the IM coal because of the volatiles. Homogeneous nitrogen conversions in a fuel rich region are more likely to partition towards N2. Moreover, the proportion of residual Ash-N produced by IM-coal is relatively high, and it is easier to convert into NO_x at a suitable reaction temperature.

According to the curves of CR_NO_x and CR_NH₃ in the premix/staged modes, the optimal ammonia blending ratio for the synergistic optimization of the flue gas pollutants in the coal/ammonia co-firing is $E_{\rm NH3} = 40$ %, at which the NO_x conversion rates reach the minimum values around 0.5 %~0.8 % as well as the relatively low NH₃ conversion rates around only 0.02 %~0.04 %. Therefore, appropriate coal/ammonia co-firing helps to improve the clean conversion of fuel-N and reduce the transformation into fuel-NO_x and residual NH₃.

From the consistency of the experimental results, it can be concluded that for coal/ammonia co-firing, the effect of coal type on the fuel-N migration is not significant, which mainly depends on the percentages of each *N*-containing component among the entire reaction paths. In

addition, the present co-firing system of the drop tube furnace could show good denitrification performance under 1200 $^{\circ}$ C for both premix/ staged modes.

3.3. SEM micromorphology of raw coal and fly ash

This study carried out SEM characterization of two types of raw coal and fly ash samples collected under the above experimental conditions to further investigate the microstructure changes inside the coal particles during the co-firing process. Fig. 10 shows the micromorphology of the raw coal and ash samples after magnification of 2000 times. The upper part is IM-coal and the lower part is GY-coal, with the results of raw coal and the ash samples obtained in premix mode and in staged mode from left to right, respectively. All ash samples are collected under the condition of 1200 °C and $\alpha = 1.2$ with the ammonia blending ratio at 40 %.

The shapes of raw coal powders on the left (a)(d) are finely divided and dispersed and the particles are scattered and in adherent to each other.

For the ash particles burnt with NH_3 under the premix mode in the middle (b)(e) of Fig. 10, the pore structure on the surface is relatively developed and adhered to each other. This is mainly due to the gas-solid heterophase reaction which continuously occurs between attached gas and coal particles. Besides, the rapid precipitation of volatiles and the heterogeneous reduction reaction of char/NO_x make the carbon structure on the coal surface significantly consumed and result in the formation of an uneven porous structure with collapsed honeycomb surface.

However, the shapes of the ash samples under the staged mode on the right (c)(f) are quite different. There are distinct fractures and cuts among the particles and it can barely observe those tiny and dense honeycomb structure. Such differences might owe to the reduction of smoke temperature as secondary air injected at the staged outlet, where the incompletely combusted coal appears collapsed pore structure inside the particle due to the rapidly changing atmosphere. Apart from that, the abundant water vapor generated by NH_3 combustion wraps the particle surface and covers its reaction active sites, which prevents the inorganic components from melting and migrating outside the surface to form rough pore structures. These inner reasons jointly lead to the agglomerates and fractures in the ash particles generated in the staged mode.

4. Conclusions

This study used the drop tube furnace to carry out experiments on the flue gas emission characteristics and fuel-N transformation rules of the coal/ammonia co-firing process with various coal types, ammonia injection modes, reaction temperatures, excess air ratios and ammonia blending ratios. In addition, the composition analysis and SEM characterization of the raw coal and ash samples under typical operation conditions were also conducted. The results include:

- (1) Significant differences of $\rm NO_x$ emission behaviors exist between the premix mode and the staged mode. The $\rm NO_x$ emission level peaks around $\rm E_{NH3}=20$ % under high temperature for the staged mode.
- (2) The reaction temperature has a decisive influence on the *N*-containing components of flue gas, especially the residual NH₃ at the furnace exit. Combined with the fuel-N conversion distribution figure, it can be attributed to: High temperature accelerates the combustion of NH₃/char and promotes the conversion from Ash-N and NH₃ to NO_x. At the same time, high temperatures (1200/ 1400 °C) out of the SNCR reaction temperature window led to much higher NO_x release than the medium temperature case (1000 °C), while the NH₃ residual content is opposite with only 0.02 % CR_NH₃ at 1400 °C and 40 % NH₃.
- (3) The decrease of excess air ratio α will aggravate the incomplete combustion of coal and promote the water-gas reaction between the unburnt carbon and H₂O which leads to a significant increase of the CO concentration. Meanwhile, the reduction reactions of unburnt NH₃ and char with NO_x under fuel-rich condition can greatly suppress NO_x generation at high ammonia blending ratio (E_{NH3} >40 %), but will cause sharply rising residual NH₃. Factors from three aspects jointly lead to the lessening of CR_NO_x as decreases.
- (4) Ammonia co-firing results of different coal types show that GYcoal input can obtain less CO emission, while IM-coal input can obtain less NO_x emission. The optimal ammonia co-firing ratio at 1200 °C is about 40 %, where CR_NO_x reaches the minimum value and CR_NH_3 is nearly zero. The fuel-N transformation ratios are barely affected by the change of coal type.
- (5) The co-firing strategy of ammonia and pulverized coal can effectively enhance the conversion rate of fuel-N to N₂ and the decarbonization ratio at 40 % NH₃ blending could reach 47.13 % and 54.30 % in the premix and staged mode, respectively. The



Fig. 10. Micromorphology of raw coal and ash samples (magnification-2000; scaleplate-10 µm).

 NO_x emission and residual NH_3 levels keep relatively low when the temperature does not exceed 1200 °C and the NO_x generation could be even lower than coal combustion if co-fired with ammonia at medium temperature.

(6) Coal/ammonia co-firing will significantly affect the micromorphology of the ash samples: in the premix mode the honeycomb surfaces of the ash are porous and adhered to each other, while in the staged mode there are obvious fractures and cuts between ash particles due to dropping local gas temperature and high ammonia concentration.

CRediT authorship contribution statement

Chenlin Chen: Methodology, Investigation, Writing – original draft, Data curation. Zhihua Wang: Conceptualization, Resources, Writing – review & editing. Runfan Zhu: Investigation, Data curation. Jiaxin Tan: Resources, Formal analysis. Yong He: Validation, Supervision. Kefa Cen: Validation.

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.

Data availability

Data will be made available on request.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (52125605) and the Fundamental Research Funds for the Central Universities (2022ZFJH004).

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