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Ammonia Co-firing with Coal: A Review of the Status and Prospects

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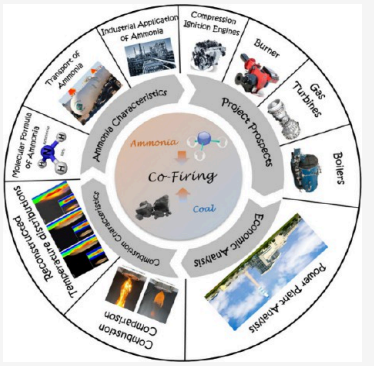
ABSTRACT: The reduction of the emissions of CO_2, especially from coal-fired power plants, is an important topic due to the caused greenhouse effect. Ammonia/coal co-firing is considered as a practical means to reduce CO_2 emissions without necessitating a significant overhaul of the existing power infrastructure, presenting a potential avenue for energy transition. Despite the promise, there exists limited research on ammonia co-firing. On the basis of ammonia applications worldwide and its fuel properties, this study begins by introducing the combustion characteristics of ammonia, addressing the challenges, and outlining the future development trends of ammonia combustion. Subsequently, an in-depth exploration of ammonia/coal co-firing is conducted, evaluating both its technical and economic feasibility. The discussion encompasses a thorough review of combustion dynamics, pollutant emissions, and the resultant impact on boilers to offer a holistic perspective on the ammonia/coal co-firing paradigm. Through a comprehensive overview, this paper strives to provide theoretical reference for the large-scale application of ammonia/coal co-firing technology in the evolving energy landscape.



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1. INTRODUCTION

CO_2 stands as a major type of greenhouse gas.[1] In 2022, global CO_2 emissions exceeded 36.8 Gt, an increase of 321 Mt compared to 2021, showing a continuing upward trend.[2] To realize "carbon neutrality", the global community has come up with a series of regulations and measures. For example, the announcements by the European Green Deal (2021) and International Maritime Organization in 2020. The former instituted stringent standards targeting air pollutant emissions from internal combustion engine vehicles while the latter introduced rigorous emission standards for offshore operations.[3] According to International Energy Agency (IEA), global CO_2 emitted from energy combustion increased by 423 Mt in 2022, of which coal-fired electricity contributed to an increase of 224 Mt (especially for emerging economies in Asia).[2] Therefore, it is very important to cut the emissions of CO_2 from the power generation sector.

To be specific, in the European Union, CO_2 emissions from the power sector have increased 3.4%, but coal consumption is not significant while the share of wind and solar power generation has increased significantly. In the United States, CO_2 emissions from electricity and heat generation have been reduced because of the increase in solar photovoltaics (PV), wind, and coal-to-gas.[2] As for China, because of a high power abandonment rate attributed to the intermittent and unstable nature of renewable, coupled with immature technology for large-scale power storage,[1,4] the electricity and heat production constituted 51.4% of the total carbon emissions in 2021, making the carbon reduction in the power sector the key to achieving overall carbon neutrality.[1] In other Asian countries, nearly 103 Mt CO_2 was caused by coal-fired power generation.[2] In Japan, the power sector relied on coal-fired power generation contributes the most CO_2, accounting for 37% of its national total.[5] To summarize, the CO_2 emission from coal-fired power plants should be taken seriously, especially in Asia.

To abate carbon emissions from coal-fired power generation, three principal methods are concerned:[6,7] carbon capture [e.g., the carbon capture, utilization, and storage (CCUS) technology[7]], the efficiency promotion [e.g., the integrated gasification combined cycle (IGCC) technology[8]], and alternative fuels (e.g., partial or full usage of ammonia[9]). Compared with the carbon capture and efficiency promotion technologies, alternative fuels, such as ammonia, emerge as one of the most feasible means of large-scale emission reduction for the coal-fired power sectors.[9−12] Notably, alternative fuels leverage existing equipment in coal-fired power plants, requiring retrofitting only for the installation of carbon-free fuel storage, transportation, and injection systems,[13] thereby mitigating development and commercialization costs (Figure 1).[1,9,14] In conclusion, ammonia/coal co-firing has application

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prospects, as described in China,[15] Korea,[16,17] Philippines,[18] Japan,[19] India,[20] and some other countries.

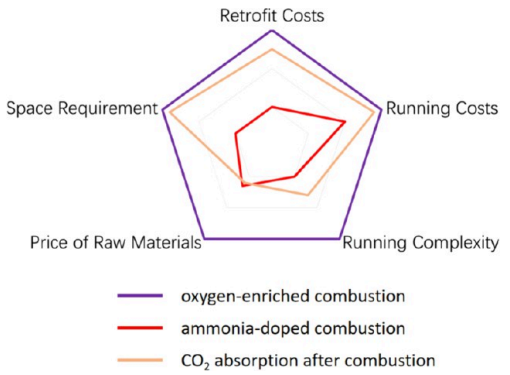

Figure 1. Comparison of the cost of CO_2 emission reduction technologies for coal-fired power stations. This figure was reproduced with permission from ref 14. Copyright 2024 Elsevier, Ltd.

Ammonia, as a noteworthy energy carrier, can be produced by consuming surplus intermittent renewables such as wind power and solar photovoltaic power. This not only fosters the development and utilization of renewables but also positions ammonia as a crucial player in advancing sustainable energy practices.[1] Furthermore, ammonia boasts several advantages, including higher energy density, enhanced safety features, facile storage and transportation, and the capacity for large-scale deployment.[1,9,21,22] Therefore, the ammonia/coal co-firing technology has been proved to be feasible. Ammonia/coal co-firing can, to a large extent, cut the produced CO_2 while improving the poor combustion performance of NH_3. Coal provides a large amount of volatiles including H_2 and hydrocarbons such as CH_4, which can promote the combustion of NH_3.[4,23] Coals with higher volatile content contribute to better combustion performance. The Levelized Cost of Electricity (LCOE) was computed by Hiraoka et al.,[24] who pointed out that coal combustion combined with carbon capture and storage (CCS) could cut down CO_2 emissions by 69%, that ammonia/coal co-firing combined with CCS could decrease CO_2 emissions by 74%, that pure NH_3 combustion combined with CCS could reduce CO_2 emissions by 90%.

Based on the aforementioned attributes, this paper presents a thorough review of ammonia combustion that is anchored in its fundamental properties. Currently, there is a dearth of reviews dedicated specifically to the topic of ammonia/coal co-firing. A list of some recent reviews is given in Table 1. The novelty of this work lies in its emphasis on ammonia/coal co-firing as the primary subject matter, offering a comprehensive analysis of the research progress and feasibility of widespread adoption of ammonia/coal co-firing in carbon-neutral environments. This paper not only delineates the properties of ammonia and the research status of ammonia-coal mixed combustion but also delves into ongoing commercial projects related to ammonia/coal co-firing. Moreover, it scrutinizes the economic viability of the ammonia/coal co-firing technology in coal-fired power plants. The overarching goal is to provide a valuable reference for future research endeavors, thereby enriching the collective knowledge base in the quest for sustainable energy solutions.

2. CHARACTERISTICS OF AMMONIA

2.1. Ammonia Toxicity. Ammonia (NH_3), even at a concentration as low as 300 ppm (parts per million), can pose a great threat to human health.[29] And prolonged exposure to concentrations exceeding 30 ppm for more than 15 min can result in lasting damage to the body.[30] Moreover, due to its lower gas density compared to air (0.66 kg/m^3 versus 1.2 kg/

Table 1. Existing Reviews on Ammonia/Coal Co-firing

year	reference	main work of the reference	contribution of this work
2021	13	① ammonia characteristic ② research status of the mixed ammonia/coal combustion ③ laboratory and commercial projects	① ammonia toxicity ② ammonia transportation ③ economic analysis ④ efficiency and ignition delay time of the co-fired systems
2023	25	① ammonia characteristic ② ammonia combustion model and mechanisms ③ NO_x mitigation strategies of ammonia combustion ④ soot emission characteristics of ammonia	① descriptions of the co-firing of ammonia and solid fuels ② specific mechanisms of NO_x emission reduction ③ economic analysis and existing demonstration
2023	26	① ammonia characteristic ② transport and storage of ammonia ③ ammonia production technologies ④ ammonia combustion mechanisms	① detailed descriptions of the co-firing of ammonia/coal ② economic analysis
2024	14	① ammonia characteristic ② research status of ammonia coal mixed combustion ③ NO_x emission ④ industrial application of ammonia/coal co-firing	① improved method of ammonia combustion ② economic analysis ③ ignition delay time of the co-fired systems
2024	27	① carbon reduction methods ② economic systems for reducing carbon emissions ③ application of ammonia in power plant ④ ammonia production methods	① economic analysis of ammonia/coal co-firing ② combustion dynamic behavior and efficiency of the co-fired systems
2024	28	① potential of renewable energy ② ammonia characteristic, production and transport ③ project of ammonia application ④ combustion impacts on thermal systems	① improved method of ammonia combustion ② ignition delay time of the co-fired systems ③ economic analysis of ammonia/coal co-firing

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Table 2. Comparison of the Characteristics of Several Gas Fuels[1,32,33]

fuel	adiabatic flame temperature (°C)	laminar flame speed (m s^{-1})	ignition delay time (s)	combustion limit (equivalence ratio)	minimum auto-ignition temperature (°C)	octane number
NH_3	1800	0.07	1.383	0.63−1.40	650	130
H_2	2110	2.91	0.051	0.10−7.10	520	>130
CH_4	1950	0.37	0.072	0.50−1.70	630	120

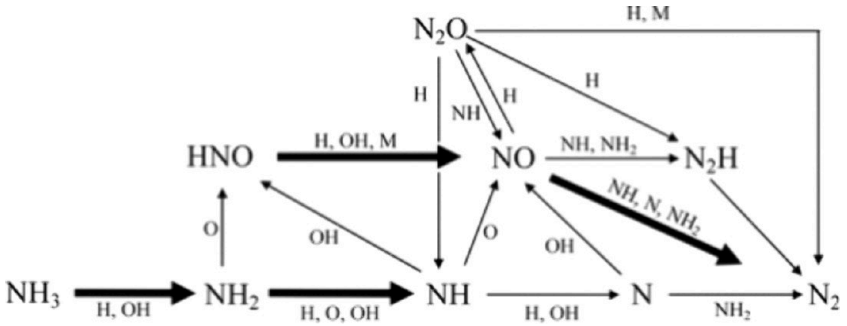

Figure 2. Reaction paths involved in the oxidation of ammonia. The primary paths are highlighted by the bold black arrows. This figure was reproduced with permission from ref 39. Copyright 2022 Elsevier, Ltd.

m^3), ammonia tends to dissipate from our breathing space, reducing the likelihood of its accumulation. However, when released in liquid form, the temperature dropping can lead to the formation of dense aerosol clouds. These clouds of ammonia, driven by wind, can spread horizontally across the ground rather than disperse vertically, posing risks to animals and plants in densely populated areas.[30] While ammonia possesses slight toxicity, its pungent odor becomes detectable at a volume fraction within the range of 5−50 ppm, considerably lower than its lethal concentration of 2000 ppm.[4]

On this basis, some regulations related to ammonia safety have been introduced to regulate the use and production of ammonia and to reduce the risks posed by ammonia leaks.[30] For example, the *Control of Ammonia Releases in Ammonia Fuelled Vessels*, which has been promulgated by International Association of Classification Societies (IACS),[31] sets the maximal concentration of ammonia at 25 ppm for ammonia felled ships, and suggests providing audible and visual alarms in places where ammonia is released.

2.2. Ammonia Flammability. Ammonia, a flammable gas, exhibits a mild oxidation process with yellow flames.[32] The color of NH_3 flame deepens with an escalating equivalence ratio.[1] Ammonia stands out as an exceptional fuel due to its carbon-free combustion, yielding nitrogen and water under ideal conditions. The comparison of the combustion performance with other gas fuels is shown in Table 2.

As can be seen from Table 2, ammonia exhibits fundamental characteristics akin to conventional fuels, including affordability, widespread availability, high combustion value, and an elevated octane number.[34] When compared to low-rank coal (around 20 MJ/kg), ammonia has a higher heat value (22.5 MJ/kg).[21,23] Therefore, ammonia can be burned directly as a fuel. Currently, ammonia is mainly used for the production of fertilizers and refrigerants. In recent years, there has been a burgeoning interest in the exploration of ammonia as a fuel source for fuel cells and engines.[35]

Complete combustion of ammonia produces N_2 and H_2O, but NO_x is also generated during the combustion process. In 1983, Miller et al.[36] reported the mechanisms for NH_3 oxidation. The NO_x generation mechanism of NH_3 differs from that of hydrocarbon fuels. Hydrocarbon fuels generate thermal NO_x in the rear parts of the flame at high temperatures, whereas NH_3 generates fuel NO_x mainly in the reaction region at the flame front, where NO accounts for more than 90% of the total.[4] The overall reaction pathways of ammonia combustion are shown in Figure 2. The reaction of the radicals such as H and OH with NH_3 to produce NH_i (i = 0, 1, 2) is the first step of ammonia oxidation. NH_3 undergoes H-abstraction by reaction $NH_3 + OH \rightleftarrows NH_2 + H_2O$ under lean conditions and by reaction $NH_3 + H \rightleftarrows NH_2 + H_2O$ under rich conditions.[37] And the reaction of NH_i (i = 0, 1, 2) with O/O_2 to produce HNO is an important step for NO_x generation;[38] therefore the amount of O, H and OH radicals in the reaction environment is decisive for NO_x generation.[33]

2.3. Ammonia Production and Market. A notable attribute of ammonia is its accessibility from intermittent and unstable renewable sources, such as tidal energy, solar energy and wind energy.[21] This makes ammonia a chemically stable alternative energy source, and its significance is further accentuated by its potential for decomposing into hydrogen for subsequent energy utilization.[21,40] Just like hydrogen, ammonia also has different color codes, which can be discerned based on hydrogen sources in the Haber−Bosch process.[28] Green ammonia means that renewable energy is used for production. Gray ammonia from the thermo-chemical conversion of fossil fuels accounts for the largest proportion of ammonia. Blue ammonia represents a combination of gray ammonia and the carbon capture, utilization and storage (CCUS) technology. And if nuclear energy is employed for electrolysis, the resulting ammonia is considered as pink ammonia.[41]

The Haber−Bosch process and the solid-state ammonia synthesis process (depicted in Figure 3) are the two most predominant methods for ammonia production.[35] As the most established technique for producing ammonia, the Haber−Bosch process, is extensively employed on a commercial scale.[42] The production sequence of ammonia involves the conversion of liquefied natural gas, methane, and coal into gaseous hydrocarbons through the steam reforming process. Subsequently, H_2 is combined with N_2 via the Haber−Bosch process to yield NH_3. The final step is ammonia extraction

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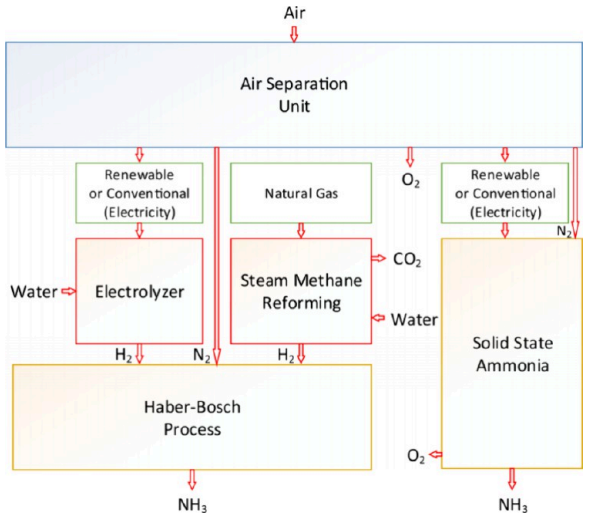

Figure 3. Two most commonly used ammonia synthesis methods. This figure was reproduced with permission from ref 35. Copyright 2019 Elsevier, Ltd.

through membrane separation, low-temperature distillation, absorption, and adsorption.[42]

It is worth mentioning that the traditional Haber−Bosch process relies on fossil fuels as a hydrogen source, resulting in substantial CO_2 emissions, especially in the steam reforming process.[43] To obtain real carbon-free ammonia fuel, methods that combine the Haber−Bosch process with the CCUS technology have been proposed.[21] These progressive methodologies involve capturing CO_2 emissions from the Haber−Bosch process and storing them underground after absorption or adsorption. This integration drastically reduces the environmental impact caused by ammonia production by preventing CO_2 release into the atmosphere, so as to mitigate climate change.[44] Additionally, captured CO_2 emissions can be utilized in applications like enhanced oil recovery or chemical synthesis, promoting the resource efficiency and circular economy principles in the industrial sector.[45]

Furthermore, there is growing interest in integrating the Haber−Bosch process with water electrolysis based on renewable electricity.[1,42] This entails electrolyzing water using energy from renewable sources like solar, wind, hydroelectric, geothermal, or ocean energy. This process produces hydrogen, a crucial material for ammonia production. Combining this hydrogen with nitrogen results in the carbon-free ammonia, providing a sustainable pathway for production and utilization.[46] Utilizing renewable electricity in this manner eliminates carbon emissions associated with traditional methods, promoting the adoption of clean energy and facilitating the transition to a greener future. Moreover, the symbiosis between renewable energy and ammonia production enables energy storage and grid balancing.[47,48] Surplus renewable electricity can be used to generate hydrogen for various purposes, enhancing energy flexibility and resilience. Overall, integrating the Haber−Bosch process with renewable-powered water electrolysis not only mitigates carbon emissions but also drives innovation, economic growth, and energy independence, thereby fostering a sustainable and resilient energy future.

It has been over 100 years since ammonia application was commercialized.[49] Large-scale production of ammonia is feasible and most can be provided by the Haber−Bosch process (about 86−96%),[42] while the remaining can be derived from the electrochemical and thermochemical processes.[50] The global production of ammonia was reported 243 Mt in 2020,[51] of which more than half was produced in Asia (Figure 4). The

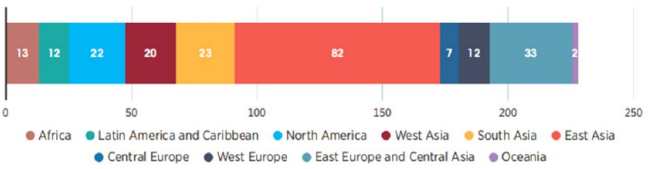

Figure 4. Ammonia production capacity by region in 2020. This figure was reproduced with permission from ref 55. Copyright 2022 International Renewable Energy Agency (IRENA).

annual ammonia market was valued at USD 91−225 billion, featuring a mature global infrastructure covering production, distribution, storage, trade, and transportation.[52] More importantly, according to IEA, the ammonia trade is expected to grow significantly by 25 times by 2050.[53] The *Green Ammonia Market* released by Future Market Insights has also forecasted an alarming growth of the global green ammonia market in the next decade, expected to be USD 14 761.3 million by 2033.[54] Therefore, benefiting from the development of water electrolysis technologies and declining costs of renewable energy, green ammonia will show economic effectiveness worldwide.

2.4. Ammonia Storage and Transportation. The safety profile of ammonia is underscored by its notably narrower explosion limit range (16−25%) as opposed to hydrogen H_2 (4−74%).[4] In addition to its safety attributes, the volumetric hydrogen content of ammonia surpasses that of liquid hydrogen by 1.7 times and exceeds that of methyl cyclohexane by 2.6 times (Table 3). Ammonia can be liquefied at −33.5 °C under standard atmospheric pressure (1 atm),[1] rendering its liquefaction more facile and energy-efficient compared to CH_4 and H_2. Consequently, ammonia stands out for its ease of reversible storage,[21] presenting a distinct advantage in terms of storage and transportation.

Stable and reliable ammonia sources and mature ammonia transportation systems are readily available for the development of the ammonia/coal co-combustion technology. Once the ammonia storage capacity reaches 150 kt, ammonia should be stored in multiple tanks.[55] When the ammonia storage scale is greater than 5 kt, ammonia is liquefied at −33 °C and atmospheric pressure, mainly stored at ports near ammonia production facilities.[56] When the ammonia storage scale is less than 1.5 kt, ammonia is stored at ambient temperature and 16−18 bar.[56]

A comprehensive transportation network for ammonia has been established worldwide, utilizing various transport means such as pipelines, rail, barges, ships, and roads.[21] For long-distance transportation, pipelines and ships are the most optimal options.[53] Marine or offshore transportation of ammonia generally uses refrigerated ammonia carriers equipped with refrigeration facilities.[57] The Middle East and Australia are emerging as major exporters of ammonia, with their trade accounting for more than 65% of the global total.[58] Nearly 18−20 Mt of commercial ammonia was expected to be transported by ship by 2020.[59] Currently, there are about 170 ships that can carry ammonia, of which 40 carry ammonia continuously.[60] According to the Ministry of Economy, Trade and Industry (METI) of Japan, it is projected that by 2050, a

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Table 3. Physical Properties of Different Hydrogen Carriers (at 1.01325 bar)

item	boiling point (°C)	density (kg m^{-3})	low calorific value (GJ m^{-3})	hydrogen content (%)	hydrogen density (kg m^{-3})	latent heat of vaporization (kJ kg^{-1})	other properties
liquid ammonia	−33.5	682.8	12.7	17.8	121.0	1377	toxic, highly corrosive, and highly soluble in water
liquid methane	−161.5	468	23.4	25.1	117.7	510	inflammable and explosive
methyl cyclohexane	100.9	769.4		6.16	47.3		combustible and irritating, its solvent toluene is toxic
liquid hydrogen	−253	70.8	8.5	100	70.8	450	highly flammable and explosive

global ammonia supply network with a capacity of hundreds of millions of tons will be established, accompanied by rapid development in the global ammonia marine transportation system, primarily consisting of ammonia-powered ships.[61]

Pipelines, less affected by weather and transportation conditions, are more efficient. Currently, the world's long-distance pipelines for liquid ammonia transportation are mainly located in the United States and Russia, such as the Ammonia System (3075 km) and the Tolyatti-Odessa pipeline (2424 km).[61] More than 2 000 000 t ammonia can be carried by these two pipelines annually. In China, there are four completed liquid ammonia pipelines with a total length of more than 100 km. The longest one is Qinhuangdao liquid ammonia pipeline, with 82.5 km and 105 000 t/a freight volume. Italy has a 74 km long pipeline.[62] In addition, there are dozens of short- and medium-distance liquid ammonia pipelines in several European Union countries, including Germany, the United Kingdom, Spain, and Poland, and most of these pipelines are less than 10 km in length.[62]

Besides, the total amount of ammonia transported by rail in Europe is approximately 1.5 million tons per year.[51] In Australia, ammonia is currently transported by truck, but ammonia-inflated blimps have been proposed as an alternative to long-distance trucking because ammonia can be liquefied and gasified to keep the blimps afloat.[51]

The well-established infrastructure for NH_3 transportation and storage, along with robust safety procedures, will significantly bolster the prominence of ammonia/coal co-firing within the energy landscape. Leveraging current equipment installed in coal-fired units further enhances its competitiveness in low-carbon transformation technologies.

3. DEVELOPMENTS AND CHALLENGES OF AMMONIA COMBUSTION

The high content of fuel-N in ammonia (82%) poses challenges to practical combustion, namely, the significant production of NO_x and the potential risk of excessive ammonia escape.[23,63] For example, NO_x emissions from some swirl burners are higher than 2000 ppm.[64] NO_x such as NO and N_2O are present in the combustion process.[65] N_2O, which has a global warming potential (GWP) more than 280 times that of CO_2 for a 20 year time scale,[28] should be concerned as a greenhouse gas.[66] Moreover, ammonia exhibits a high latent heat of evaporation, measuring 1370 kJ/kg, contributing to its poor ignition performance.[67] The suboptimal characteristics of ammonia, including low flame propagation speed and adiabatic flame temperature, coupled with a narrow flammability limit range, contribute to its poor flame stability and low combustion efficiency.[23] In order to address these challenges and enhance combustion stability, various strategies such as the high-temperature air preheating combustion, oxygen-rich combustion, swirl flow combustion and co-combustion have been proposed.[32,68]

3.1. High-Temperature Preheating Combustion.

High-temperature preheating combustion is one of the ways to ameliorate the poor combustion performance of ammonia. The stable non-premixed pure ammonia combustion laminar flame was detected by Chen et al.[69] through NH_3 preheating (see Figure 5). With the increase of the temperature, the concentration of OH rose fastest among all radicals, and its chemiluminescence enlarged the blue flame region. Moreover, within the temperature span of 593 to 740 K, the NO, NO_2, and unburned NH_3 all decreased to levels below 20 mg/m^3 (Figure 6). The main factor behind this phenomenon is the

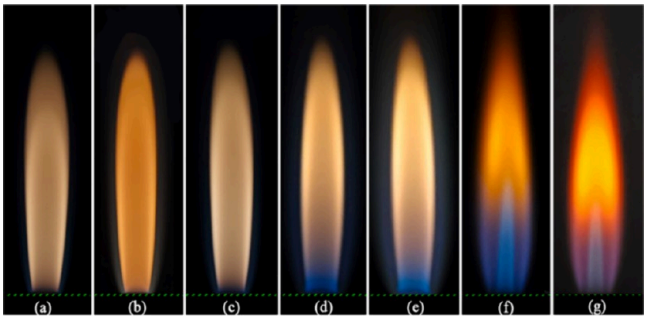

Figure 5. Visual representations of flames at various preheating temperatures: (a) 593 K, (b) 623 K, (c) 653 K, (d) 683 K, (e) 713 K, (f) 743 K, and (g) 773 K. This figure was reproduced with permission from ref 69. Copyright 2022 Elsevier, Ltd.

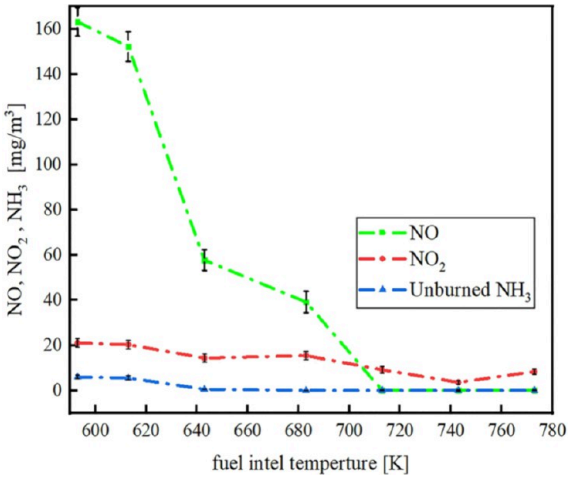

Figure 6. Effect of preheating temperatures on the emissions of pollutants under 200 mL/min NH_3. This figure was reproduced with permission from ref 69. Copyright 2022 Elsevier, Ltd.

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enhanced chemical reaction rate caused by high preheating temperature, leading to an augmented concentration of O, H, and OH radicals,[70] which were evidenced to be important in the production and consumption of NO.[69] Notably, the N + NO ⇔ N_2 + O reaction rate increased 85.9% from 623 to 773 K.[69]

Giancarlo et al.[71] explored the relationship between preheating and the release of NO_x. Under mixture equivalence ratios (ϕ) = 0.6 condition, in the temperature range 300−900 K, the concentration of NO_x ranged from 200 to 1000 ppm. If ϕ was larger than 1, NO_x emissions reduced as the preheating temperature increased, with concentration remaining below 10 ppm at 900 K. Therefore, increasing the preheating temperature under oxygen-rich swirl conditions is a feasible measure that can intensify the reaction, lead to the decomposition of a large amount of NO_x, and reduce the formation rate of NO_x.

3.2. Oxygen-Rich Combustion. In addition to the above-mentioned temperature adjustment, oxygen-rich combustion technology can effectively enhance the combustion of NH_3 as well.[32] Shrestha et al.[72] studied the oxygen-dependent laminar flame speed of ammonia, demonstrating a linear growth in laminar flame velocity with oxygen content. The maximum laminar flame speed at temperature 298 K was found to be around 20 m/s, with an equivalence ratio of around 1.1 and an oxygen content of 30%. Through the sensitivity analysis, the branching reaction O_2 + H = OH + O rose most as O_2 content improved, which dominated the reaction under oxygen-rich conditions.

Mei et al.[73] delved into the $NH_3/O_2/N_2$ combustion and found that oxygen enrichment can reduce the buoyancy effect of ammonia/air flame and make the flame shape more spherical (Figure 7). From 21 to 50% oxygen content, the laminar burning velocity (LBV) rose from less than 10 m/s to more than 30 m/s. Moreover, the increase in oxygen content did not change the main combustion reaction pathway. However, the ability of H radicals to extract H atoms from NH_3 was more than three times higher at an oxygen content of 45% compared to air combustion conditions. The augmentation of oxygen content primarily improved the thermal effect and elevated the amount of free radicals like H and OH.[73] For this reason, the reactivity of the mixture was enhanced, leading to an increase in laminar flame speed.

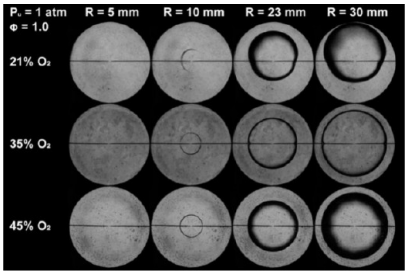

Figure 7. Schlieren photography documented stoichiometric $NH_3/O_2/N_2$ flames with the varied oxygen content from 21 to 45% at Pu = 1 atm. This figure was reproduced with permission from ref 73. Copyright 2019 Elsevier, Ltd.

3.3. Swirl Flow Combustion. Numerous relevant works have been reported on NH_3 combustion with swirl burners.[64,71,74−79] In swirl burners, high-temperature gas and active free radicals circulate back into the low-pressure zone of the burner, ensuring continuous ignition of the gas freshly entering the combustor.[4] The recirculating gas flow enhances the flame stability and prolongs the reaction time,[80] enhancing fuel mixing[81] and stabilizing the combustion over a wide range of equivalence ratios.[82] The swirl burner, commonly combined with the air-staged technology is most widely applied in ammonia combustion, especially in ammonia/coal co-combustion and gas turbine combustion.[4]

Hayakawa et al.[64] applied a swirl burner model to investigate the ammonia/air premixed flames. The square liner and higher swirl number would shrink the stable flame region (Figure 8).

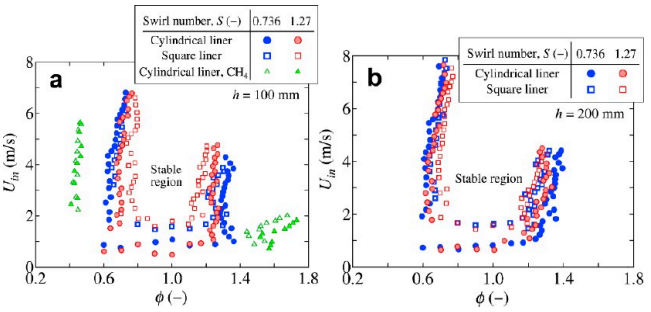

Figure 8. Map of the flame stability of ammonia/air premixed flame in the swirl burner: (a) liner length, h = 200 mm; (b) liner length, h = 100 mm. This figure was reproduced with permission from ref 64. Copyright 2017 Elsevier, Ltd.

This is mainly due to the characteristic length and speed change of the flame recirculation structure. In terms of emission, there is only NO emitted under lean conditions, at about 2000 ppm. Under the rich combustion condition, the emission of NH_3 and H_2 rose sharply while the emission of NO dropped to a very low level. This is probably because of the selective non-catalytic reduction of NO (SNCR, thermal DeNO$_x$)[83] and the effect of NH_i (i = 2, 1, 0).[84] Tang et al.[85] found that when the equivalence ratio reached 0.7, the ammonia swirl flame became unstable. However, with the help of plasma, the flammability limit was extended to 0.43. It is mainly because plasma can trigger ammonia dissociation by electron impacts to produce more NH_i (i = 2, 1, 0)[86] and then more OH are created by NH_2 + NO reaction.

3.4. Staged Combustion. This method involves implementing the rich-burn/quick-quench/lean-burn (RQL) process by precisely controlling the equivalence ratio.[4] NO_x formation is suppressed by the reduction reaction of ammonia in the rich combustion stage, and unburned fuel can be consumed in the lean combustion stage, keeping both ammonia and NO_x at a low level at the outlet.[33,87] Okafor et al.[88] analyzed the pollutants generated by premixed ammonia/air in a MGT high swirl combustor. They obtained a minimum NO_x emission of 42 ppm at inlet temperature of 298 K, pressure of 0.3 MPa, and the equivalent ratio of the main combustion zone of 1.1. Li et al.[89] used chemical reaction network (CRN) to investigate the NO_x emission behavior in a gas turbine's RQL-stage combustor when burning ammonia. They found that the NO_x emission could drop to 16.5 ppm when the oxygen content reached 40% in the fuel-rich stage. Therefore, this method can effectively avoid the equivalence ratio range associated with significant NO_x production.

Furthermore, Namsu et al.[90] formulated a CRN model to investigate ammonia combustion under the fuel stage (FS) and air stage (AS) conditions. It has been found that AS is suitable for fuel-rich primary combustion zones and secondary

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Table 4. Some Ammonia/Coal Co-firing Projects Worldwide

country	year	power plant/unit	scale (MW)	corporation	ammonia ratio (%)	reference
Japan	2017		10	IHI Corporation	20	101
	2017	Mizushima Power Station, Unit 2	156	Chugoku Electric Power	0.6−0.8	102
	2021	Hekinan Thermal Power Station, Unit 5	1000	JERA Co., Inc. IHI Corporation	small volume	103
	2024	Hekinan Thermal Power Station, Unit 4	1000	JERA Co., Inc. IHI Corporation	20	104
China	2022	Yantai Coal Power Plant	40	China Longyuan Power Group Corporation Limited	35	28
	2023		100−300	Wanneng Tongling Power Generation Co., Ltd.	10−35	28
India	2022	Adani Power Mundra Coal Fired Power Plant		IHI Corporation Kowa Company, Ltd. Adani Power Limited	20	20
South Korea	2023	Shin Boryeong Power Plant	1000 550	Ministry of Industry, Trade and Energy	20	28

combustion zones with short residence time,[90] so that the emission of NO, N_2O and NO_2 can be close to 0.[87,91] For example, 200 ppm of NO emission was obtained at global equivalence ratio (ϕ_G) = 0.7, primary zone equivalence ratio (ϕ_P) = 1.2, and secondary combustion zone residence time of less than 1 s. By contrast, FS applies when the primary combustion zone is under lean conditions, necessitating controlled staged air to achieve DeNO$_x$.[92] For example, at ϕ_G = 0.45 and ϕ_P = 0.7, NO emissions could be reduced to 100 ppm.

3.5. Co-combustion. As mentioned above, in addition to H_2, CH_4 and other gas fuels,[93−96] ammonia-coal blending is also a way to improve the combustion performance of ammonia.[4,23] In accordance with the calculations, competition between ammonia and coal combustion can increase the ammonia combustion rate while decreasing the coal combustion rate. However, due to the synergistic effect between ammonia and coal, the intermediate products generated during coal combustion can promote ammonia decomposition and oxidation.[97]

Cui et al.[98] conducted ammonia-coal mixing experiments using a flat flame burner. They discovered that at higher ammonia concentrations, the individual pulverized coal particles were subjected to more heat, and the heating rate of the pulverized coal particles increased, resulting in more intense pulverized coal combustion, increased flame brightness, and shorter ignition delay time. When the concentration of pulverized coal reached 1.1 kgc/kga, its ignition delay time was more than three times that of 0.1 kgc/kga. Xu et al.[10] conducted relevant experiments in a 600 MW boiler. Due to the carbon neutrality of NH_3, a 5% increase in NH_3 co-firing rate was found to reduce the CO_2 emissions of the boiler by 24.08 t/h. The higher H content of ammonia also caused the water content in the flue gas to increase by more than 50% (compared with pure coal) at the 20% ammonia doping condition.

Thus, ammonia-coal mixed combustion stands out as a highly promising technology. It not only facilitates the reduction of the substantial CO_2 emissions associated with coal combustion,[10,24] but also enables the stable combustion of ammonia flame.[98,99]

4. ECONOMIC FEASIBILITY OF AMMONIA/COAL CO-FIRING

4.1. Technical Feasibility. Ammonia/coal co-firing is currently demonstrated in coal-fired power plants,[13] especially in Southeast Asian countries.[100] Some of the representative projects worldwide are listed in Table 4.

China, as a developing country, has also made great progress in ammonia/coal co-firing. In September 2021, the Anhui Energy Collaborative Innovation Center, jointly established by the Institute of Energy, Hefei Comprehensive National Science Center, and the Anhui Energy Group Co., Ltd., launched the Demonstration Project of Comprehensive Utilization of Ammonia for Power Generation. In January 2022, experiments of the industrial-scale co-firing with ammonia were successfully performed in Shandong, China. As reported, it was the world's first pilot-scale (40 MW) operation with 35% ammonia co-firing.[28] The operation successfully achieved a burnout rate of NH_3 as high as 99.99% and a total reduction of 950 million tons of CO_2 emissions per year.[105] Within the 0−25% ammonia doping range, the volume fraction of unburned NH_3 in the exit flue gas was within 12×10^{-6}, the volume fraction of CO was lower than 160×10^{-6}, and the mass concentration of NO_x (lower than 200 mg/m^3) was not significantly different from that of pure coal. Additionally, the minimum content of unburnt carbon was 9%, which was lower than that of the pure coal condition (about 13%).[106] Furthermore, in April 2023, Wanneng Tongling Power Generation Co., Ltd.. demonstrated the safe and stable co-firing of 10−35% ammonia in a 100−300 MW power system with a 99.99% burnout rate of NH_3 and lower than 2 ppm of NH_3 escape rate. The boiler efficiency was comparable to that of the coal-fired conditions, and the NO emissions can be controlled and reduced.[28] The same year in June, a forum was organized by Tsinghua University to discuss the schedule of the National Key R&D Plan for hydrogen or ammonia co-firing. In July 2023, the MW-level full-scale ammonia/coal co-firing pilot-scale experiment was performed by Xi'an Thermal Power Research Institute Co., Ltd., based on its self-developed key technologies of enhanced combustion and NO_x control.

In terms of ammonia/coal co-firing technology, Japan is a leading country. In 2017, through the adjustment of the swirl intensity of the secondary air, the co-firing experiments were successfully conducted on a 10 MW combustion system by Japan's IHI Corporation (IHI) with blending ratio of 20%.[101]

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Table 5. Experimental Results Using a 10 MW_{th}-Class Combustion Test Furnace[107]

	O_2 (vol %, dry)	NH_3 (ppm, 6% O_2)	CO_2 (vol %, 6% O_2)	CO (ppm, 6% O_2)	UC (wt %)	NO (ppm, 6% O_2)
coal firing	2.5	0	13.2	15	3.0	101
20% NH_3 co-firing	2.6	0.4	10.6	13	3.6	136

This could result in stable combustion and similar pollutant gas emissions to those observed in pure coal combustion (Table 5).[107] Following the introduction of ammonia doping, the unit efficiency exhibited a slight decline, yet remained above 80%.[108] In the same year, the co-firing test with 0.6−0.8% NH_3 at a consumption rate of 450 kg/h was also successfully reported on a 156 MW coal-fired power unit by Chugoku Electric Power in Japan.[102] Subsequently, in October 2021, a series of small-volume ammonia-doped experiments were jointly launched by Japan's JERA Co., Inc. (JEAR) and IHI in Hekinan Thermal Power Station Unit 5 (1000 MW) to validate the practicability of co-firing ammonia.[104,109] On the basis of these small-volume experiments, 20% ammonia/coal co-firing is expected to be carried out at the Hekinan Thermal Power Station Unit 4 (1000 MW) in March 2024.[110] The emissions of unburned NH_3 are approximately zero, and the emissions of other gas components are shown in Figure 9. At

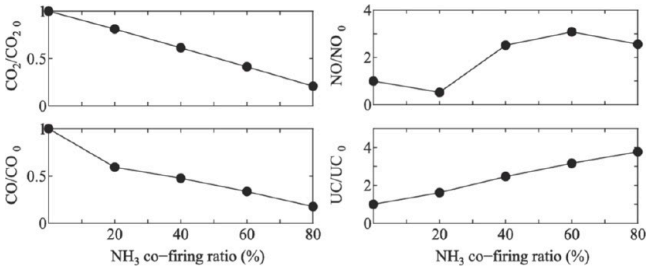

Figure 9. Effect of varying NH_3 co-firing ratio on normalized emissions of CO_2, CO, NO, and unburnt carbon in ash (UC). This figure was reproduced with permission from ref 107. Copyright 2022 Elsevier, Ltd.

20% ammonia doping, the emissions of CO, CO_2 and NO are lower than that of the coal-only condition, and the unburnt carbon increases slightly but remains within the controllable range.[107] This would be the world's first large-scale demonstration test, aimed at confirming whether stable combustion, nitrogen oxide control and the combustion adjustment in response to fluctuations in electricity demand can be achieved.[110] After that, JERA will continue to explore the technology to rise the substitution rate to 50% and even 100%.[110] All the low-efficient coal-fired power plants will be closed by Japan's JERA by 2030, and NH_3 co-firing will be introduced by Japan's JERA to all of its power generation systems by 2040.[13]

Besides, IHI and JERA are trying to expand the technology to other countries.[100] They plan to help Malaysia to reduce greenhouse gases and reach carbon neutrality by 2050.[100] In 2021, *IHI* launched a feasibility study on ammonia co-firing technologies and economics at coal power stations in Malaysia with PETRONAS Gas & New Energy Sdn. Bhd. and TNB Power Generation Sdn Bhd.[111] The joint feasibility study was finished in 2023,[112] and IHI has cumulatively provided Malaysia with 7100 MW of installed boiler capacity.[100]

"India−Japan Clean Energy Partnership" was announced by the Indian and Japanese governments on March 19, 2022.[20] Nowadays, a feasibility analysis on 20% ammonia/coal co-firing and 100% ammonia combustion has been initiated by Adani Power Limited, IHI and Kowa Company, Ltd. at the Mundra power plant in Gujarat, India.[113] Adani Power Limited is dedicated to India's ambition of achieving net-zero emissions by 2070.[113]

South Korea has paid attention to ammonia/coal co-firing since 2022.[114] In the year 2023, 20% ammonia blending was conducted in ultra-supercritical pulverized coal boilers and circulating fluidized beds.[115] Ammonia/coal co-firing with a ratio of 20% will be implemented in coal power plants by 2024.[114] The co-firing of ammonia/coal is estimated to be implemented in more than half of Korean coal power stations as early as 2030.[116]

In Vietnam, as the coal-fired power generation rate is as high as 30%, ammonia mixing may contribute to Vietnam's carbon neutrality.[117] On December 5th, 2022, Korea and Vietnam entered into a Memorandum of Understanding (MOU) to collaborate on the key mineral supply chain. The two countries agreed to add ammonia/coal co-firing technology to existing power industry cooperation.[117]

A number of researchers have questioned and challenged the ammonia/coal co-firing technology, citing a slight drop in exit flue gas temperature[10,118,119] as an example. A lower value of flue gas temperature means that more radiation heating surfaces need to be placed in the furnace, which in turn

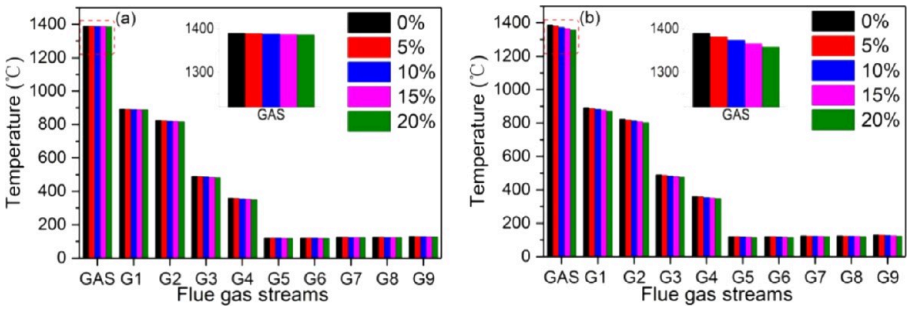

Figure 10. Temperature distribution at various points throughout the boiler system. GAS and G1 to G9 denote the flue gas from the furnace outlet to the rear: (a) identical AFT scenarios and (b) identical EAC scenarios. This figure was reproduced with permission from ref 10. Copyright 2022 Elsevier, Ltd.

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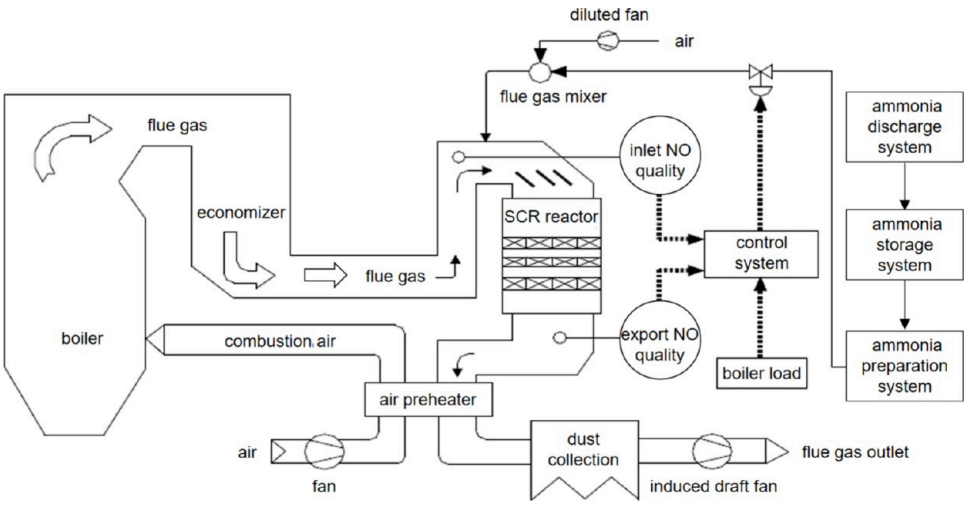

Figure 11. Flowchart of a SCR DeNO$_x$ system in thermal power plants.

leads to uneconomical heat transfer and steel consumption.[119] However, the temperature drop of flue gas is relatively small. To illustrate, the findings of Genichiro et al.[10] demonstrate the efficacy of 20% ammonia doping in a 600 MW coal-fired power plant. This led to a reduction of 31.5 °C (less than 2.5%) in flue gas temperature at boiler exit, using the identical excess air coefficient (EAC) method (Figure 10b). Furthermore, using an appropriate combustion method, such as the identical adiabatic flame temperature (AFT) method, the temperature of the steam and gas was approximately consistent with that of pure coal combustion, resulting in a 3.7 °C (less than 0.5%) flue gas temperature drop (Figure 10a). The slight variation in flue gas temperature at the furnace exit indicated that excessive heat and slag accumulation would not be worse with ammonia co-firing, which would be beneficial to boiler safety.[2]

The application of ammonia/coal co-firing in coal-fired power plants has been demonstrated to be a viable approach, and further pilot projects are being conducted in many countries. Nevertheless, there are numerous other areas that require further improvement, including technology development,[108,120] materials global procurement,[120,121] the emission reduction,[106,118,122,123] unstable electricity supply[124] and so on. In order to achieve the desired outcomes, the combined efforts of both government sectors and scientific research institutions are essential.[120]

4.2. Economic Feasibility. *4.2.1. Feasibility Analysis of Combustion Facilities.* China owns mature coal combustion technology and equipment, favoring ammonia/coal co-firing. Currently, unit modification mainly involves two aspects: the first is the modification of the burner, such as the addition of ammonia supply piping as well as ammonia preheating equipment;[106] and the second is the ammonia supply system, which includes the ammonia storage tanks, vaporizers, and ammonia delivery piping.[108]

In the work of Genichiro et al.,[108] the air for combustion was provided by the primary air fan and the blower. During the blending process, ammonia is a substitute for part of the coal, reducing the primary air for conveying pulverized coal. To compensate for this reduction and to ensure fuel combustion, the amount of air supplied by forced draft fan increased, and the total amount of the air required for combustion remained constant in the design. Therefore, the total amount of the flue gas involved in ammonia co-combustion increased slightly due to the input of NH_3. However, no modifications were needed for the primary air fan, blower or the induced draft fan because of the excess capacity in the design specifications of the combustion system. Furthermore, Hanaoka et al.[120] and Genichiro et al.[10] verified that the temperature of the steam and gas closely resembled that observed during traditional coal combustion, suggesting that modifications to the heat transfer section may not be necessary.[108]

Moreover, since NH_3 is commonly employed in selective catalytic reduction (SCR) reactions (Figure 11), its unloading and storage systems are already in place. Consequently, nearly all the necessary facilities for ammonia/coal co-firing are readily available in current coal-fired units, including primary air fans, gas-air heaters, induced draft fans, etc. The installation of ammonia injection equipment is the primary requirement for ammonia/coal co-firing.[108] To sum up, the existing infrastructure of coal-fired power plants underscores the low retrofitting costs associated with ammonia co-firing.

On this basis, Li et al.[125] calculated the retrofit cost of ammonia doping combustion for a 600 MW supercritical unit (Figure 12). The cost of the burner and the ammonia supply piping were not changed despite the increase in ammonia doping rates. Therefore; the unit retrofit cost was found to decrease with the increase of the blending ratio of ammonia.

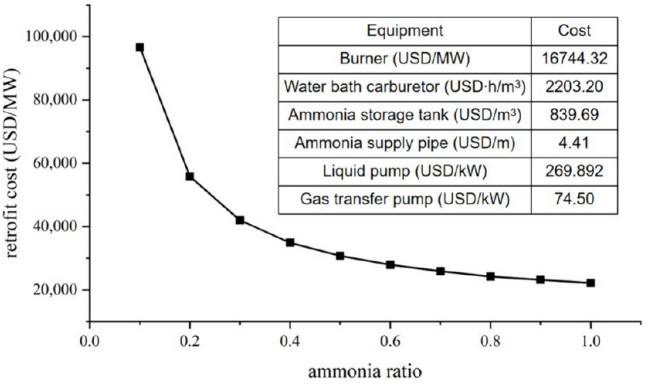

Figure 12. Equipment cost. This figure was reproduced with permission from ref 125. Copyright 2022 Chinese Society of Power Engineering.

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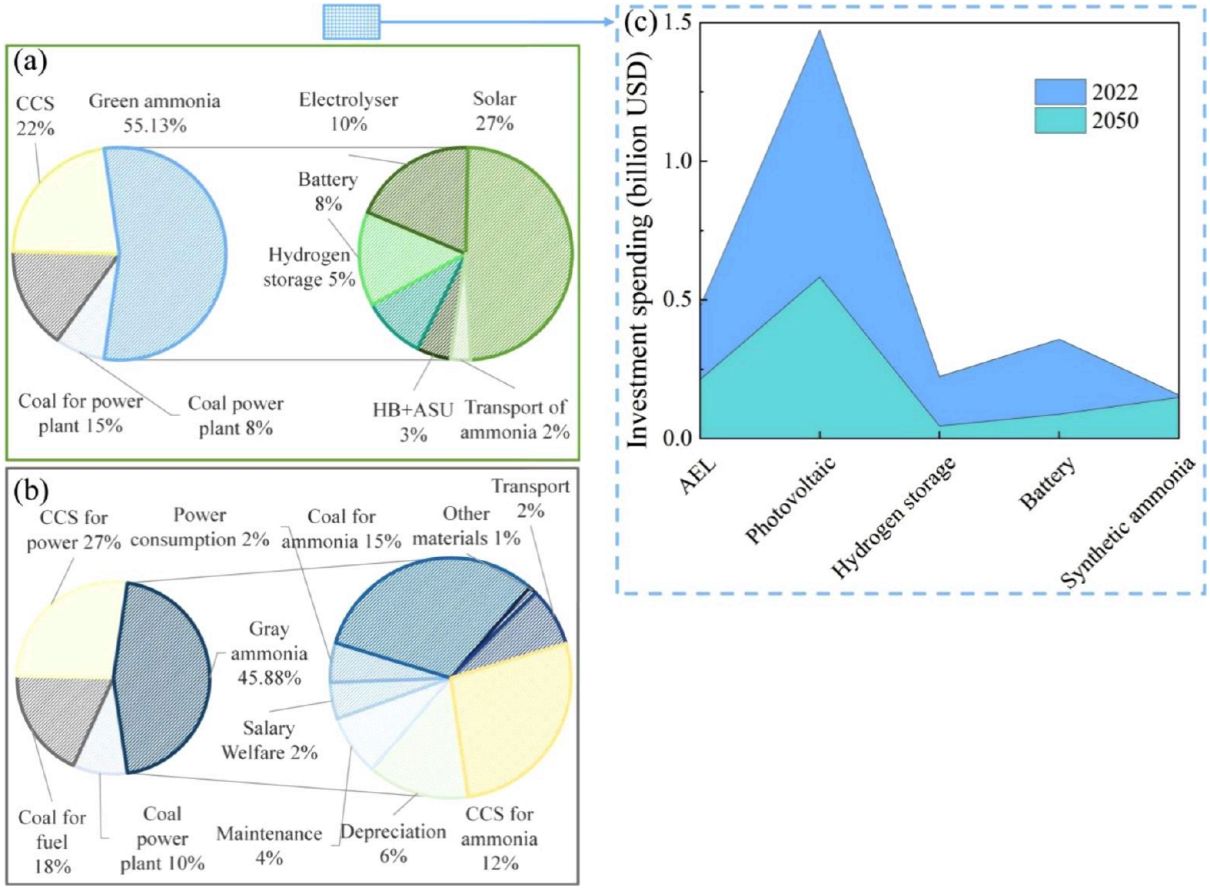

Figure 13. (a) Share of GE + CCS system (30%) in total operating costs for 2022, (b) share of GA + CCS system (30%) in total operating costs for 2022, and (c) variations in the capital allocated to the green ammonia synthesis unit (30%). This figure was reproduced with permission from ref 126. Copyright 2023 Elsevier, Ltd.

From a LCOE perspective, the effect of plant infrastructure retrofitting cost is low in comparison with fuel costs.[126]

4.2.2. Economic Feasibility of Ammonia/Coal Co-firing. Sun et al.[126] conducted a life cycle assessment (LCA) and analyzed the LCOE for 600 MW industrial coal-fired systems, taking into consideration the entire fuel chain from production to transportation to co-firing. In the case of pure coal, the LCOE was 0.042 USD/kWh. However, when the gray ammonia used in ammonia/coal co-firing was produced by coal water slurry gasification, the coal consumption increased, resulting in increased LCOE.[126] When 83 USD/t of standard coal was used,[127] the LOCE of 30% gray ammonia co-firing was 0.044 USD/kWh. This indicates that the use of gray ammonia does not effectively reduce CO_2 emissions but leads to increased costs.

Ammonia synthesis following hydrogen production from nuclear energy (often referred to as "pink ammonia") is considered feasible but has not been widely promoted due to concerns raised by Bicer et al.[128] regarding its radioactivity and potential threats to the environment and health. While advancements in technologies such as fusion reactors may pave the way for potential applications of pink ammonia in the future, it is currently too early to discuss its economic viability.[28]

Consideration of the CCUS technology, an emerging solution for high concentration CO_2, provides a very good perspective on the economic analysis of the blue ammonia/coal co-firing.[126] As evidenced in ref 11, the expenses associated with CO_2 reduction by using CCUS was estimated to be 27.54−134.54 USD/t. The current coal cost in Japan has been calculated to be 16.7 US cents/kWh by Hiraoka et al.[24] when considering the construction and operation of power plants. Therefore, 20% blue ammonia co-firing results in a cost of 18.0 US cents/kWh, which includes the cost of ammonia production and transportation and CCS.

As for green ammonia, Sun et al.[126] found that when the 600 MW coal power unit applied 30% green ammonia co-firing, the LCOE was 0.110 USD/kWh. The green ammonia was produced by the electrolysis technology using an alkaline electrolyzer (278 USD/kW).[127] Li et al.[125] estimated the levelized cost of power generation with ammonia-coal blending. Under the existing conditions in China, the expense of ammonia-coal blended power generation experienced a notable rise alongside higher ammonia doping ratios. At a green ammonia price of 516.40 USD/t and a carbon price of 20.66 USD/t, the pure ammonia combustion cost reached about 24.80 US cents/kWh, which is more than three times that in the pure coal case. When the ammonia doped ratio is 10%, the price of carbon-free ammonia is reduced to 206.56 USD/t and the carbon tax reaches 91.02 USD/t, the cost of ammonia doped power generation can be equal to that of coal-fired power generation.

Co-firing of ammonia (except gray ammonia and pink ammonia) is considered as an ideal solution to reducing the emission of CO_2. However, the cost is crucial in large-scale promotion. According to levelized power calculations, the cost

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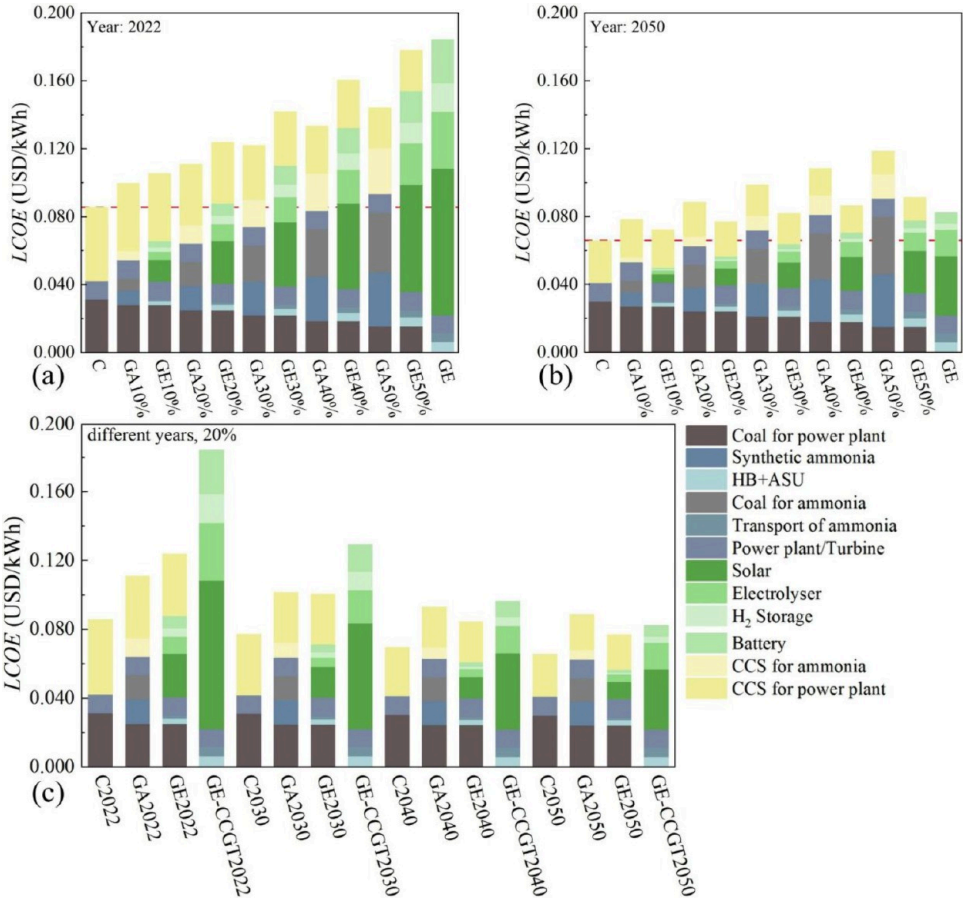

Figure 14. Analysis of the LCOE components under various scenarios for (a) 2022 and (b) 2050 and (c) analysis of the LCOE components under various scenarios in different years with a 30% share. This figure was reproduced with permission from ref 126. Copyright 2023 Elsevier, Ltd.

reduction of hybrid ammonia-coal generation depends on two factors: the price of carbon-free ammonia and the carbon tax.[125] Unfortunately, the exorbitant price of NH_3 hinders its future development and popularization.[129] Figure 13 illustrates the annual operating costs of gray ammonia (GA) + CCS technology and green ammonia (GE) + CCS technology, with the cost of ammonia being the primary contributor, accounting for 45.88 and 55.13%, respectively.[126] To achieve a competitive edge in ammonia/coal co-firing, a significant reduction in the price of green ammonia is necessary,[129] primarily through technological breakthroughs.[119]

For the time being, blue ammonia combustion still emits a small amount of carbon dioxide (absorbs 80% CO_2)[21] while green ammonia combustion features truly zero carbon emissions. Considering both ammonia production and policy implementation, it is anticipated that the share of green ammonia will be one of the largest of all ammonia types in the future, leading to its widespread application in various industries including processing, power generation, and heating.[21] Moreover, with expected technological advancements, green ammonia may gain economic advantages in the future (Figures 14 and 13c).[126] The economic feasibility of co-firing was re-evaluated by Ding et al.[9] with the consideration of the cost of coal, the production price of "green ammonia", and the price of carbon capture while excluding the cost of transportation and storage. Their findings revealed that, in the case of a 20% reduction in CO_2 emissions, coal blending with ammonia became more economically favorable than CCUS when the price of electricity used to produce "green ammonia" was lower than 1.37−2.47 US cents/kWh. Therefore, our focus will be on green ammonia.[130]

Based on data from Chile and Argentina, Armijo et al.[131] estimated the cost of flexible production of green ammonia using solar power and wind power. Under the condition of 80% flexibility, the price of green ammonia produced using the Haber−Bosch process was estimated at 462 to 710 USD/t. Li et al.[125] applied the levelized carbon-free ammonia formula to estimate the cost of NH_3 produced using hydropower electrolysis. They took into account the cost of equipment modification, the cost of energy consumption for equipment operation, the cost of routine maintenance of equipment, the cost of human resources, the cost of storage of ammonia and oxygen, the cost of transportation of ammonia, and the revenue from the sale of oxygen. Based on the renewable energy tariff of 3.64 US cents/kWh, the cost of carbon-free ammonia is 514.30 USD/t, which is much higher than the cost of gray ammonia in China (about 302.96 US cents/t) in the same year.

Electricity price is the primary factor affecting the price of green ammonia.[132] In the cost of carbon-free ammonia synthesis, energy consumption accounts for the largest proportion, at about 53%, so the use of renewable energy generation will greatly affect the cost of ammonia synthesis.[125] Figure 15a illustrates a pronounced escalation in the cost of green ammonia with the change in electricity price.[132] When the electricity price is lower than 1.40 US cents/kWh, the fuel cost of green ammonia becomes more economical compared to gray ammonia and natural gas. When the green ammonia is generated by waste electricity (i.e., the electricity price is 0 US

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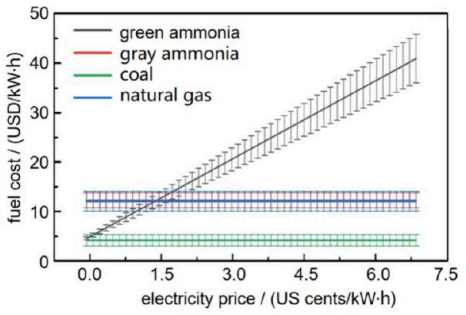
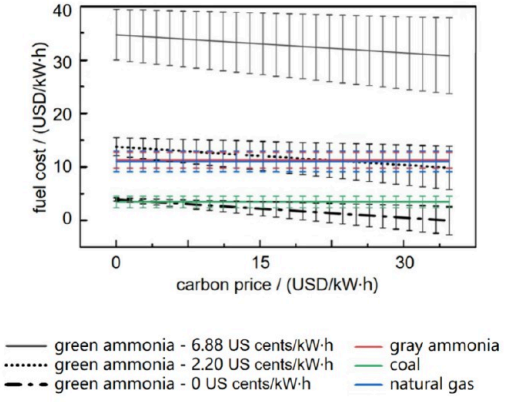


(a) The relationship between fuel costs and electricity price



(b) The relationship between fuel costs and coal price

Figure 15. Change trend of the cost of different fuels with the change of electricity prices and coal prices. This figure was reproduced with permission from ref 132. Copyright 2023 Chinese Society for Electrical Engineering.

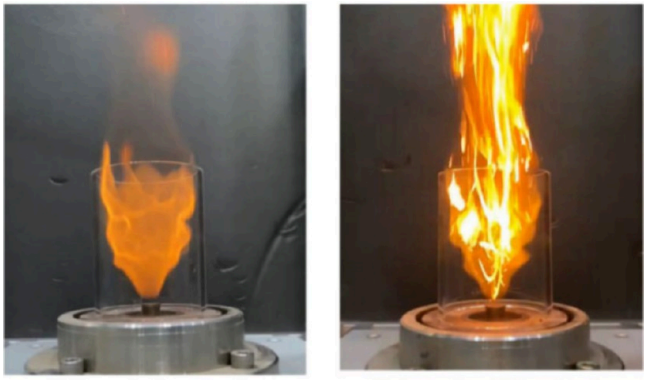
cents/kWh), the fuel cost of green ammonia is approximately equal to that of coal. Sun et al.[126] supported this opinion and thought the abandoned wind and solar resources would be great choices. As can be seen from Figure 15b, if green ammonia is produced by surplus electricity from renewable energy sources (the electricity price is 2.20 US cents/kWh), the substitution of green ammonia for gray ammonia and natural gas becomes economically feasible when the carbon price rises above 23.41 USD/t.

In summary, ammonia/coal co-firing stands out as an effective approach for reducing CO_2 emissions within the current energy framework. The decreased cost of ammonia and the increased carbon taxation are poised to facilitate the commercial adoption of ammonia/coal co-firing. Looking ahead, Tan et al.[132] have underscored the potential for synthesizing ammonia using surplus or abandoned electricity from renewable energy sources, which can be stored at distributed energy storage stations. This suggests promising avenues for the future development of ammonia co-firing.

5. CURRENT RESEARCH ON AMMONIA/COAL CO-FIRING

Ammonia/coal co-firing is a cutting-edge topic. The following section is a comprehensive review of the current achievements in ammonia/coal co-firing, highlighting aspects such as combustion performance, flame propagation characteristics, the emission of NO_x, unburned carbon, unburned ammonia, etc.

5.1. Combustion Dynamic Behavior. *5.1.1. Flame Shape and Flame Intensity.* Co-firing experiments of ammonia and coal were performed by Niu et al.[106] in a 40MW coal-fired boiler to explore the flame morphology at the outlet of the burner. An intense and bright flame was formed under 0−25% co-firing ratios, indicating the stable combustion of ammonia and coal. The flames for ammonia burning and ammonia/coal co-firing are shown in Figure 16. Attributed to



(a) Ammonia-air combustion (b) Ammonia-coal-air combustion

Figure 16. Flames observed in a burner of 5 kW_{th} capacity: (a) flame of 100% NH_3 combustion and (b) flame of 30% NH_3/70% coal co-firing. This figure was reproduced with permission from ref 13. Copyright 2021 Multidisciplinary Digital Publishing Institute.

the long combustion time of char and volatiles, the flame resulting from ammonia/coal co-firing is longer and brighter than that of the ammonia combustion.[13] Cui et al.[98] investigated the blending combustion of ammonia and coal, with coal concentrations ranging from 0 to 1.08 kgc/kga. They found that ammonia would burn rapidly when preheated at high temperatures, and that the heat released further preheated coal particles. As a result, the pyrolysis rate of the coal increased, leading to improved local gas equivalence ratios around the coal and a reduced risk of fire extinction during combustion. At the same time, by reducing the concentration of pulverized coal was reduced, more heat could be used by individual pulverized coal particles, resulting in more complete coal combustion and a brighter flame.

The role of co-firing ratio on flame shape in a single swirling burner has been demonstrated by Zhang et al.[118] (see Figure 17). At 10 and 20% ammonia blending ratio, the flame was in a normal swirl shape. Beyond a co-firing ratio of 40%, the internal recirculation zone of the flame was thoroughly pierced by the high-velocity NH_3 jet,[107,118] and the flame shifted from a normal vortex into a long and thin one.[107,118] According to the conclusion drawn by Ma et al. from their experiments in a 20 kW sedimentation furnace,[133] the injection position of ammonia had little effect on the flame shape.

5.1.2. Flame Temperature and Flame Burning Speed. The feasibility of large-scale application of ammonia/coal co-firing is contingent upon addressing challenges related to the ignition difficulty and low flame burning speed of ammonia. Lots of works have been published to address these two main challenges. It was found that, the ignition temperature of the blending fuel, would rise with the enhanced NH_3 co-firing ratio.[98,134] Gong et al.[135] carried out a series of ammonia/coal co-firing experiments using a flat flame burner. It was found that for premixed combustion, an increasing ammonia co-firing

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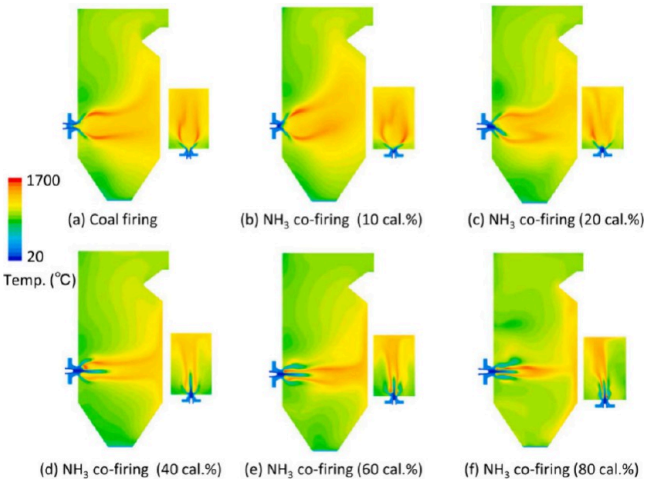

Figure 17. Impact of NH_3 co-firing ratio on gas temperature distribution. This figure was reproduced with permission from ref 118. Copyright 2020 Elsevier, Ltd.

ratio (0−100%) correlates with a higher combustion temperature (about 1500−1600 °C). For non-premixed combustion, elevating the ammonia loading from 0 to 20%, the temperature decreased from 1500 to about 1425 °C. Further increase in the ammonia doping ration had no significant effect on the temperature.

When ammonia is mixed with traditional hydrocarbons, the heat release speed and flame speed of the blending fuel are higher than those of pure ammonia.[33,136] Xia et al.[137] carried out an experiment with a spherical chamber and found that in ammonia-poor environments, the flame propagation speed of the reaction front in ammonia/coal co-firing exceeded that observed in pure NH_3. While in ammonia-rich environments, the opposite was true. For example, when the ammonia equivalent ratio was 0.4, the propagation speed was about three times greater compared to burning pure NH_3. If NH_3 equivalence ratio was 1.3, the propagation speed was about 0.4 times lower compared to burning pure NH_3. This is mainly due to the heat absorption of the unburned coal, the intense radiation emitted by the glowing flame, and the competitive effect of the furnace's local equivalence ratio. More accurate data were obtained by Hadi et al.,[138] who showed that the volatile content of the coal could also significantly affect the combustion rate of ammonia/coal co-firing for all turbulence intensities. At a low equivalence ratio, high volatile coals exhibited a flame speed in ammonia/coal co-firing that was three times higher than pure coal and twice as fast as pure NH_3; for low volatile coals, however, the combustion rate of the ammonia/coal was almost the same as that of pure NH_3. Furthermore, researchers found that the flame propagation velocity increased with increasing turbulence intensity,[137,138] and at a turbulence intensity of 1.29 m/s, the flame propagation velocity was about 1 m/s higher than that in the non-turbulent case as the turbulence enhanced the mixing of heat and matters and increased the surface area of the wrinkled flame.

5.1.3. Ignition Delay Time. Cui et al.[98] found that coal ignition is pivotal in the combustion of ammonia-coal mixtures through flat-flame burner experiments. Studies have indicated a positive correlation between the ignition delay time of ammonia-coal blends and the pulverized coal concentration when ammonia injection rates remain constant.[139,140] However, at pulverized coal concentrations below 0.67 kgc/kga, the substantial presence of ammonia led to heightened consumption of oxygen and heat from the environment. Consequently, this phenomenon impedes the declining rate of coal ignition delay time (Figure 18).[98]

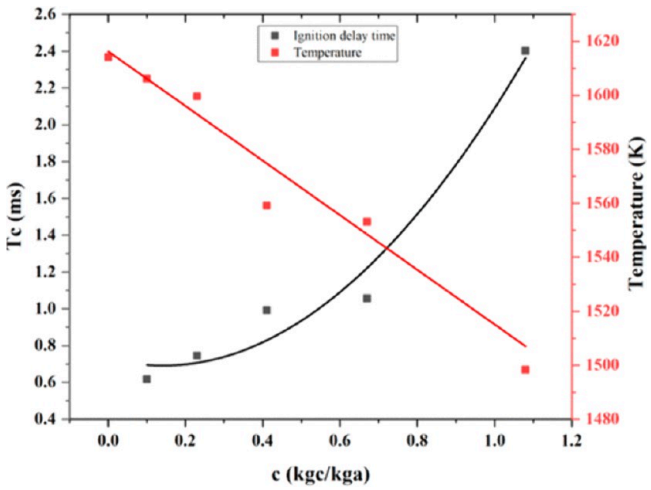

Figure 18. Effect of the concentration of coal on the ignition delay time. This figure was reproduced with permission from ref 98. Copyright 2024 American Chemical Society.

Chen et al.[67] conducted experiments using a high-temperature furnace and reported that a certain NH_3 co-firing ratio could promote coal devolatilization and thus enable quick ignition of coal. They conducted a comparative analysis of ammonia/coal co-firing and pure coal combustion at 1400 and 1500 °C. This comparison revealed a reduced ignition time (about 5−10 s) for ammonia/coal co-firing over the whole range from 0 to 100% ammonia doping.

Zhang et al.,[99] employing CFD, found that increasing the proportion of ammonia blending could meliorate the ignition performance of ammonia/coal co-combustion using a 0.58 MW pilot scale with moderate or intense low-oxygen dilution (MILD) combustion furnace. Their findings suggested that elevating the ammonia ratio enhances the ignition performance by promoting early reactions between ammonia, volatile components, and oxygen, consequently bolstering gas-phase combustion and facilitating earlier particle ignition. Conversely, a reduction in the coal ratio diminishes the energy available for coal ignition. Notably, as the ammonia blending ratio increased from 0 to 50%, there was a substantial reduction in ignition time of 52.1% and a reduction in ignition temperature of 33%.

Wu et al.,[141] utilizing an optical measurement system in a two-stage flat flame combustor, concluded that the pulverized coal flame is usually located behind the surface of the ammonia flame. When the oxygen volume fraction behind the flame in the inner zone was 0%, the ammonia flame increased the heating rate of the pulverized coal and promoted the pyrolysis of the pulverized coal. However, the ammonia combustion competes for oxygen with coal combustion. The effects of the two counteracted each other, so that the ammonia doping did not have a significant effect on the ignition delay time, which was about 20 ms. However, when the oxygen volume fraction behind the flame in the inner zone increased to 10 or 20%, the increase of the ammonia doping ratio significantly shortened the ignition delay time. Under the condition of pure ammonia

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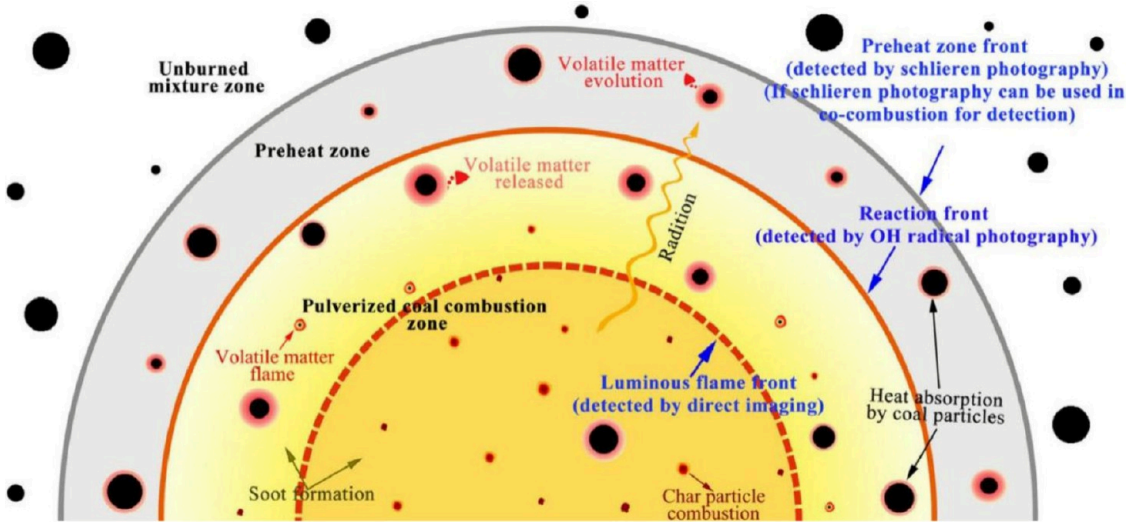

Figure 19. Amount of heat absorbed by radiation and convection at walls. This figure was reproduced with permission from ref 137. Copyright 2020 The Combustion Institute.

with an oxygen volume fraction of 20%, the ignition delay time decreased to less than 10 ms, indicating that the contributed combustion of volatile component induced by the increased temperature primarily drives the ignition advancement.

5.1.4. Radiation. Xia et al.[137] employ a distinctive fan-stirred constant volume chamber to conduct an experiment. Figure 19 shows the flame structure of a one-dimensional ammonia/coal co-firing. Within the preheating region, small coal particles were subjected to the heat transfer effect of the reaction front and the radiation effect of the luminous flame in the pulverized coal combustion zone, liberating a large amount of volatiles. Furthermore, the radiation from the luminous flame promoted the flame propagation speed in the preheat zone during co-firing. The high temperature soot particles in the luminous flame performed a crucial function in generating substantial radiation in ammonia/coal co-firing,[142] while the coal particles themselves only had a minor impact on radiation.

A MILD combustion technology was applied in ammonia/coal co-firing, as proposed by Zhang et al.[99] In comparison to the exclusion of particle radiation, the cases that included particle radiation caused more temperature drops (Figure 20). It can be observed that, at ammonia doping ratios of 0, 10, 20, 30, 40, and 50%, the temperature decreases by 4.8, 4.3, 4.0, 3.6, 2.9, and 2.8%, respectively. It is evident that an increase in ammonia blending decreases the concentration of coal particles and thus reduces the extent to which particle radiation affects the flame temperature. The temperature of 50% ammonia blended case is 5.9% lower than the pure coal case when only gas radiation is applied, and 8.5% lower when gas and particle radiations are considered, indicating that gas radiation exerts a more significant effect in determining the flame temperature.

Cui et al.[98] posited that alterations in convective and radiative heat transfer would affect the heating rate of coal particles when ammonia/solid fuel compositions differed. Zhang et al.[118] employed Ansys Fluent 15.0 to investigate the ammonia/coal co-firing in a low NO_x swirl burner produced by IHI Corporation. The results indicated that as the ammonia blending is increased from 0 to 60%, the total amount of heat absorbed gently dropped as a result of the weakened particle radiation (Figure 21). Nevertheless, an increase in the ammonia blending ratio from 60 to 80%

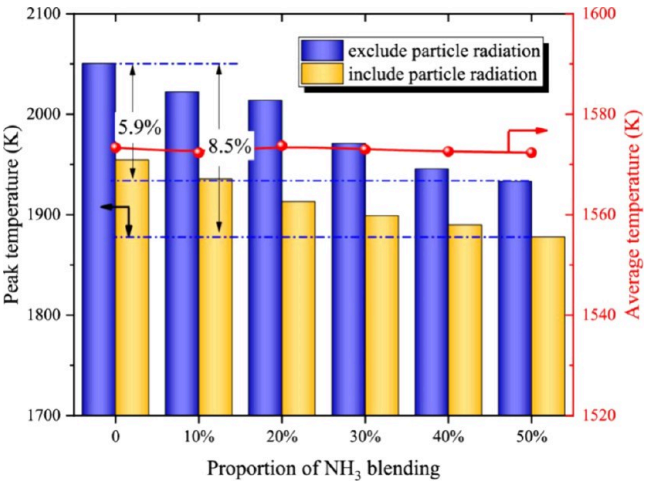

Figure 20. Peak and average flame temperatures throughout the furnace. This figure was reproduced with permission from ref 99. Copyright 2022 American Chemical Society.

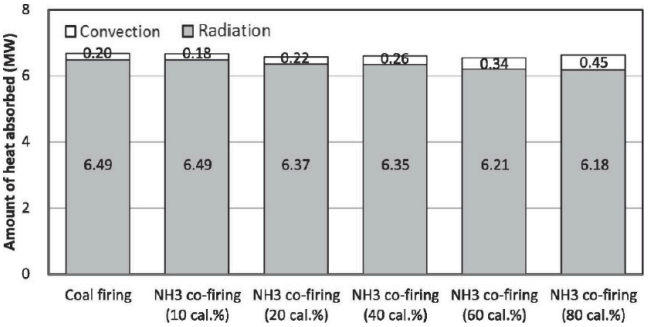

Figure 21. Amount of heat absorbed by radiation and convection at walls. This figure was reproduced with permission from ref 118. Copyright 2020 Elsevier, Ltd.

resulted in a rise in the heat absorbed. This phenomenon may be explained by the increased quantity and velocity of the gas in the burner, which has resulted in an increase in the proportion of convective heat transfer with the increase in

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ammonia. This increase is greater than the decrease in radiative heat transfer.

Chen et al.[119] considered that flame radiation is mainly caused by the triatomic gases (mostly CO_2, H_2O, SO_2), fly ash and coal particles. Their experiments in a 600 MW supercritical coal-fired boiler corroborated the findings of Zhang et al.[118] As NH_3 increases, the triatomic gas concentration rose, whereas the concentration of fly ash and coal particles declines. Upon reaching a 50% ammonia blending ratio, the volume ratio of triatomic gases increased by 3.4%, and the concentration of fly ash and coal particles decreased by 14.6 and 3.3 g/m^3, respectively. This resulted in a 8.2% reduction in flame emissivity.

Chen et al.[143] demonstrated that the flame temperature and coal particle burn-up rates are suppressed by the thermal radiation characteristics of coke, fly ash and soot particles at a high ammonia doping rate. This can be illustrated by the gradual increase in unburnt carbon content as the ammonia doping rate increases, as shown in Figure 22. Furthermore, this

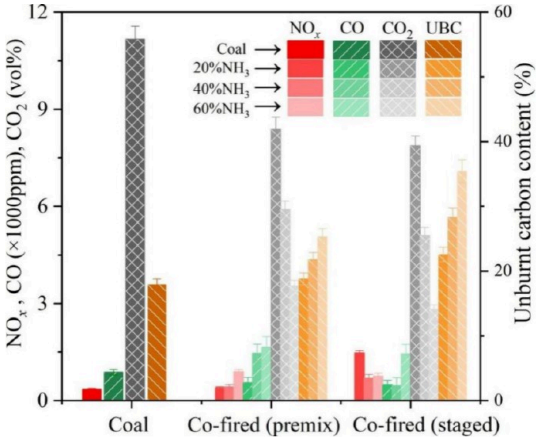

Figure 22. Amount of heat absorbed by radiation and convection at walls. This figure was reproduced with permission from ref 143. Copyright 2022 Elsevier, Ltd.

research team proposed that, in terms of boiler safety, it is crucial to consider the superposition of the furnace radiation and the maximum flue gas velocity at the center in order to prevent excessive thermal loading of the boiler.

Aim at mitigating the weakened effects of radiation, Zhu et al.[38] conducted a literature review and concluded that porous media burners (PMB) were a promising option. PMBs can deliver a consistent temperature curve, low NO_x emission and improved radiation efficiency. However, this technology is currently used mainly in the field of ammonia/hydrogen/air co-firing.

5.2. Pollutant Emission during Ammonia/Coal Co-firing. *5.2.1. NO_x Emission.* For mixed combustion of ammonia and coal, the nitrogen compounds in the flue gas are more complex. Cui et al.[98] investigated NO_x emission from ammonia/coal co-firing at different pulverized coal concentrations and at different heights above the burner (HAB) on a flat flame burner (Figure 23). In the experiment, NO_x mainly contained three gases, N_2O, NO, and NO_2, among which the proportion of NO in NO_x was more than 94%. In the latter phases of combustion, there was a rapid decrease in N_2O generation, mainly due to the reducing effect of unburned ammonia. For NO_2, the pronounced combustion of char in the reducing atmosphere caused the decrease of NO_2 concentration in the later stages. It has been found in the experiment that when the coal concentration decreased, the oxygen concentration increased, resulting in easier formation of NO and NO_2, so the oxygen concentration is the dominating factor affecting NO_2 production.[144] The conversion of N_2O to NO_2 was also facilitated by OH radicals, which were formed from the breakdown of H_2O, an important product during NH_3 combustion.[145]

The basic properties of coal are one of the factors that affect the NO_x emission from ammonia/coal co-firing. With the help of the thermal gravimetric analyzer, Gong et al.[135] observed that H_2O produced from NH_3 combustion could promote the gasification reaction of char, which would result in a looser pore structure of the char/coal, contributing to the release of small molecules. Therefore, in the range of 40−100% ammonia blending ratio, NO_x emission was 2000 mg/Nm^3 higher compared to the pure coal case. The fuel-dependent NO_x emission characteristics have been investigated by Fan et al.[146] on the fixed-bed and they found that the heterogeneous reduction of NO was largely affected by the pore structures. WCW char with the largest porosity (775.0 m^2/g pore surface, 0.489 cm^3/g pore volume) showed a maximum NO reduction efficiency of more than 90%, while SMX char with the worst porosity (335.1 m^2/g pore surface, 0.119 cm^3/g pore volume) had a maximum efficiency of only 80%. Enriched micropores possessing broad pore volume and surface area could improve the adsorption capacity of coals. Consequently, more NH_3 could be adsorbed on the surface of coals to promote the overall NO reduction reaction. Wu et al.[141] applied a flat flame burner and found that an increase in ammonia blending ratio indeed increased coal fragmentation (Figure 24). This may be due to the fact that the free radicals generated from the ammonia gas-phase reaction promote volatile matter reactions and coal/coke surface reactions, damaging the surface of coal particles.

Apart from the structure of coal, the intrinsic mineral composition can also affect the NO_x emissions in ammonia/coal co-firing. The impact of additives on the reduction of NO was investigated by Fan et al.[146] on a high-temperature fixed bed. It was found that NH_3 could enhance the NO-char heterogeneous reactions within the range of 950−1350 °C, while the contents of Fe_2O_3, Fe_3O_4, and Cu_2O in the fly ash could increase the NO reduction efficiency by nearly 30%. Chen et al.[147] burned demineralized coal and Fe-impregnated coal respectively with ammonia on a high-temperature fixed bed to investigate the role played by Fe on NO emission. The NO reduction efficiency of ammonia/Fe-impregnated-coal co-firing was slightly below that of ammonia/demineralized-coal co-firing (Figure 25), indicating that Fe may bind to the amino group to generate Fe−N complexes, which can inhibit NO reduction.

Comparatively speaking, more effort has been paid on the impact of the ammonia co-firing ratio. Niu et al.[106] found that the co-combustion of NH_3 and coal was stable and efficient in a 40 MW_{th} boiler when the co-firing ratio of NH_3 was less than 25%. In the absence of overfire air (OFA), the mass concentration of NO_x in the boiler was found to increase monotonously with the rise of NH_3 co-firing ratio, from 440 mg/m^3 at pure coal to 884 mg/m^3 at 25% NH_3 co-firing ratio. Provided that 20% OFA, the mass concentration of NO_x would first increase and then decrease as the NH_3 doping ratio increases. The addition of ammonia at a 20% blending ratio

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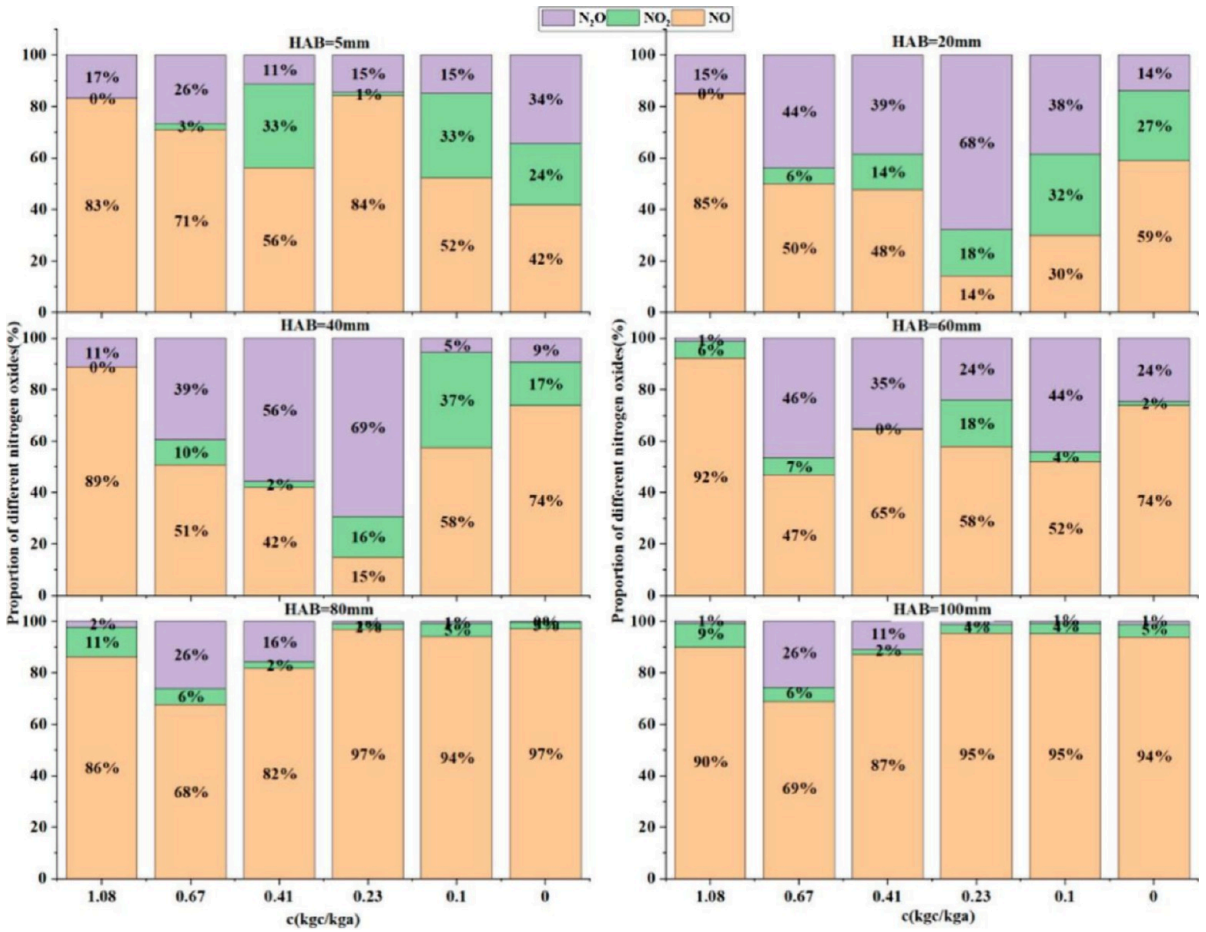

Figure 23. Proportion of different nitrogen oxides. This figure was reproduced with permission from ref 98. Copyright 2024 American Chemical Society.

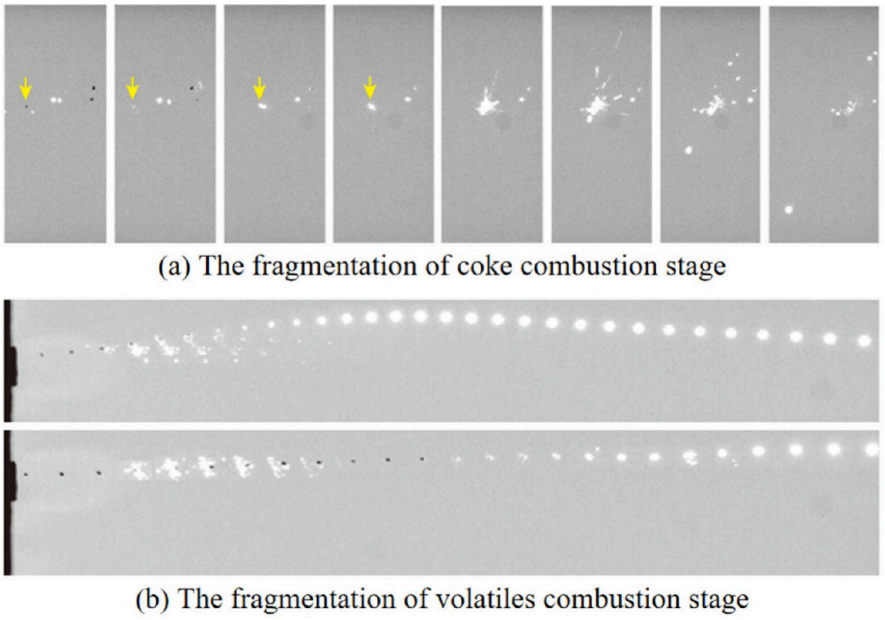

Figure 24. Two typical coal particle ignition modes. This figure was reproduced with permission from ref 141. Copyright 2023 China Coal Research Institute

resulted in a reduced mass concentration of NO_x at 20% compared to pure coal combustion, where NO_x levels were measured at 140 mg/m^3.

The blending combustion of ammonia and coal in a 1000 MW coal-fired boiler was simulated utilizing ANSYS Chemkin-Pro by Ishihara et al.,[107] who suggested that NO emission

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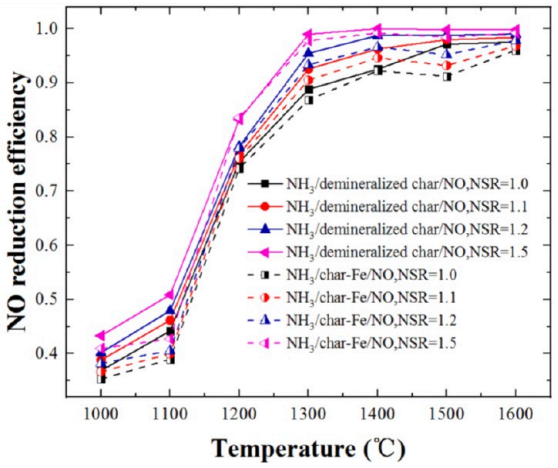


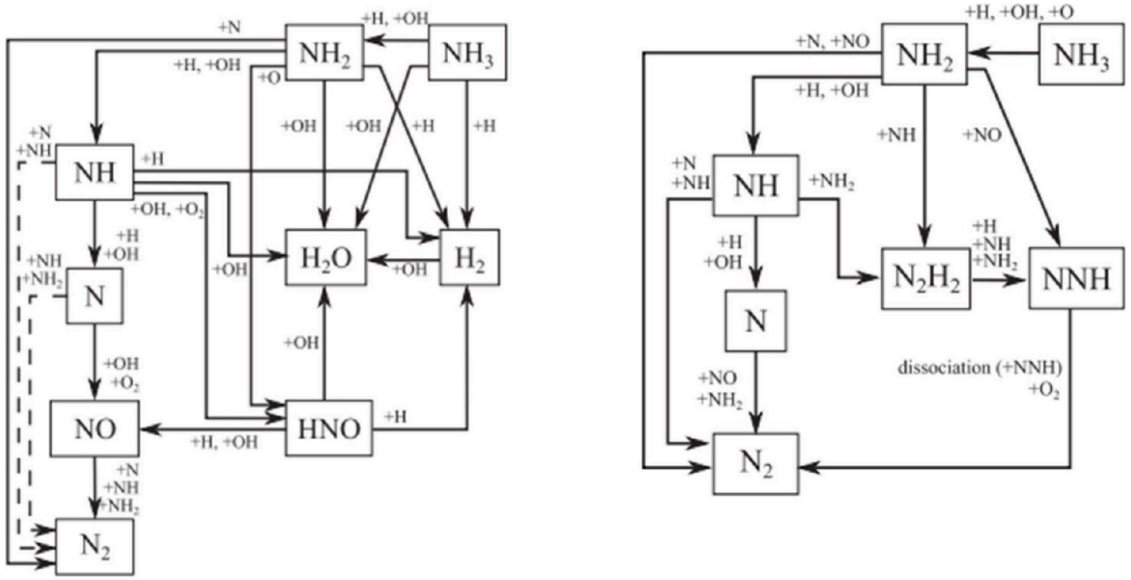
Figure 25. Effect of Fe in the NH_3/char/NO reaction system (char-Fe is iron impregnated char). This figure was reproduced with permission from ref 147. Copyright 2022 Elsevier, Ltd.

increased monotonously within 20 to 60% co-firing ratio range, while at the higher ratio of 80% NO emission declined to the level of 40% co-firing. They further explored different reaction paths of NH_3 under different ammonia-doped ratios (Figure 26).[107] At 20% and 80% co-firing, the reactions $NH_3 + H \rightarrow H_2 + NH_2$ and $NH_3 + OH \rightarrow H_2O + NH_2$ were dominant. However, at 40% and 60% co-firing, $NH_3 + O \rightarrow NH_2 + OH$ and $NH_2 + NH_2 \rightarrow NH_3 + NH$ were the most significant. To be specific, at 20% ammonia doping ratio, NH_3 was dissociated to produce fuel-NO in a 2000 K furnace. At 80% ammonia doping ratio, NH_3 was dissociated to generate fuel-NO and N_2 [through NH_i (i = 0, 1, 2)], resulting in lower NO emissions. At 40 and 60% co-firing ratio, the active paths did not include NO, but $NH_i + NH_i$ (i = 0, 1, 2) became important.

Zhang et al.[118] obtained the same results when simulating the 8.5 MW coal-fired boiler with eight swirl burners. It was demonstrated that the emissions of NO_x at the outlet of the boiler followed a pattern of initially increasing and then decreasing as the rise of the co-firing ratio. Notably, NO_x was mostly generated in the flame zone.[148] Furthermore, the fluctuation of NO_x with ammonia co-firing ratio was clarified: For high co-firing ratios, unburned NH_3 from the combustion zone reached the downstream post-flame reduction zone, thereby reducing NO_x emission through $DeNO_x$.[107,118]

A search of the available works indicated that temperature and excess air coefficient (oxygen concentration) are two important factors affecting the NO_x emission. Fan et al.[146] found that within the experimental temperatures range of 950 to 1350 °C on a fixed-bed reactor, the NO emission after 500 ppm ammonia doping was at least about 50 ppm higher than with pure coal, which proved that more NH_3 was converted to NO through oxidization. Jiang et al.[149] conducted ammonia/coal co-firing experiments and demonstrated that in the range of 0−10% blending ratio, as the temperature increased, the time to peak NO decreased gradually from about 50 s to less than 25 s. Figure 27 shows the release of NO, which rises and then falls with temperature increase. It is mainly due to the fact that when temperature exceeded 1200 °C, the rate of formation of amino free radicals from unburned ammonia started to increase, which contributed to NO reduction reactions.

To elucidate the effect of oxygen concentration, an ammonia co-firing test was carried out in a 40 MW_{th} coal-fired boiler by Niu et al.,[106] which revealed that with the drop of oxygen content, the NO_x mass concentration decreased remarkably. The decrease of oxygen content from 4.24 to 2.35% would cause the concentration of NO_x to drop by about 36%. Wang et al.[134] obtained the same results in their experiments. When the operating oxygen content dropped from 7.74 to 1.52%, the NO_x concentration decreased by 2806 ppm under 25%



(a) 20% and 80% co-firing. (b) 40% and 60% co-firing.

Figure 26. Pathways associated with the decomposition of NH_3 (dashed lines are the paths in the case of 80% co-firing). This figure was reproduced with permission from ref 107. Copyright 2020 Elsevier, Ltd.

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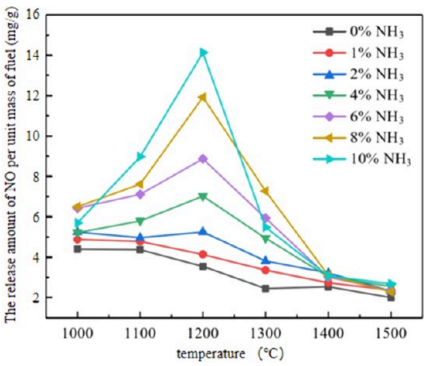

Figure 27. Total released NO per unit mass of fuel. This figure was reproduced with permission from ref 149. Copyright 2023 Chinese Society for Electrical Engineering.

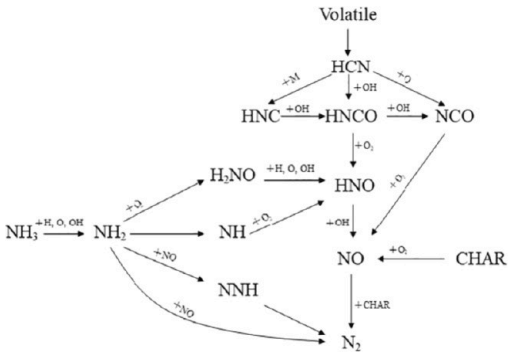

Figure 28. Reaction path involved in the interconversion of NH_3-N and coal-N. This figure was reproduced with permission from ref 152. Copyright 2022 Elsevier, Ltd.

ammonia blending ratio. They also proposed an optimal excess air coefficient of 1.12 to 1.14 employing a one-dimensional flame furnace.[134] The increase of the excess air coefficient enhanced combustion, but induced the reaction of $NH_3 + O_2 \rightarrow NO + H_2O + 0.5H_2$,[133] increasing NO_x concentration sharply. Furthermore, Fan et al.[146] found that NH_3 was conducive to NO_x reduction when it is injected to the combustion zone under extremely low-oxygen or oxygen-free conditions. When the oxygen content was 0−4% in the air-stage area, the reduction efficiency of NO increased first and then decreased as the temperature rose from 800 to 1500 °C. At 0% oxygen content and 1300 °C, the highest reduction efficiency was close to 50%. Early exposure of ammonia to air before its combustion could adversely affect NO control. To sum up, lower oxygen concentrations reduce NO_x emissions, partly because of incomplete fuel combustion and partly because unburned NH_3 reduces some NO_x to N_2.[106]

Generally, the mechanism of the co-combustion of ammonia/coal is complex and involves a variety of reactive substances and free radicals such as NH_i (i = 0, 1, 2), HNO, HNCO, and NCO.[150,151] Wang et al.[152] explained the reason behind the first increase and subsequent decrease in NO emissions when ammonia/coal co-firing happens under non-staged combustion conditions. Tar has been acknowledged as a main carrier of coal nitrogen. When the temperature is up to 1400 K, tar undergoes rapid pyrolysis to produce HCN.[153,154] HCN, one of the products in reactions R6 and R7, is an important intermediate N species delineated by the De Soete mechanism.[155] HCN can be converted to HNO by the following reactions at high temperatures:[152]

$$HCN + OH \rightarrow HNCO + H \quad (R1)$$

$$HNCO + O \rightarrow HNO + CO \quad (R2)$$

HNO plays a pivotal role in regulating the concentration of NO under fuel lean conditions. As the ammonia doping ratio increased from 10 to 50%, the rate of HNO → NO could be escalated by 20%.[152] Figure 28 shows the dominating reaction paths involved in the conversion of N-containing species in ammonia/coal co-firing, highlighting the role of increased ammonia in promoting the NHO group production.[152] However, when the ammonia doping ratio continued to rise, NH_3 would increasingly compete for oxygen, thereby suppressing HNO production (as per reaction R2). At the same time, the rates of NO reduction reactions also surged, with the primary reactions as follows:[152]

$$NH_2 + NO = N_2 + H_2O \quad (R3)$$

$$NH_2 + NO = NNH + OH \quad (R4)$$

$$NH + NO = N_2O + H \quad (R5)$$

In addition, recombination of NO_x with C_xH_y and CO is of great importance in the N-containing cycle and is the basis for fuel staged combustion technology.[156] The two main N-containing products, NO and N_2, can be reduced by recombination with hydrocarbons (reactions R6 and R7).[155,157] As for CO, it can be reduced at high temperatures by mineral-catalyzed reduction in char through reaction R8.[156]

$$C_xH_y + NO \rightarrow HCN + \text{products} \quad (R6)$$

$$C_xH_y + N_2 \rightarrow HCN + NH_i \quad (i = 0, 1, 2) \quad (R7)$$

$$CO + NO \rightarrow CO_2 + 1/2N_2 \quad (R8)$$

5.2.2. Unburned Carbon and Unburned Ammonia. The discrepancy in temperature field, concentration field, and particle field caused by the injection of NH_3 may affect coal combustion and burnout and further contribute to unburnt carbon in the fly ash. Meanwhile, inappropriate organization of the combustion process may also bring about emission of unburned NH_3, which must be avoided.[1,148]

Ishihara et al.[107] explained that ammonia oxidation consumed more O_2, inhibiting the consumption of carbon, and the value of unburned ammonia at 80% doping was close to four times that of pure coal combustion. Jiang et al.[149] suggested that, as the NH_3 blending rate rose, the amount of unburned NH_3 increased, but NO reduction reaction consumed NH_3, so that the total NH_3 amount at the outlet was small. This was validated by Ishihara et al.[107,148] through numerical calculations. They concluded that NH_3 escape was less than 1% of the total NH_3 injected, and the injected NH_3 would be depleted near the combustor.[118] In a 1000 MW coal-fired boiler, the main NH_3 consuming position was found to shift with the co-firing ratio. Most ammonia was consumed in the flame zone at blending rates of 20, 40, and 60%. While at 80% co-firing ratio, most ammonia was consumed in the post-flame region.[107] Furthermore, oxygen content was also found to affect ammonia escape. In 40 MW coal-fired units, the volume fraction of unburned NH_3 increased from 3.1 to 138 ppm as the working oxygen decreased from 4.24 to 2.35% because of decreased NH_3 oxidation degree in the early stage caused by an oxygen-poor environment.[106] In general, NH_3

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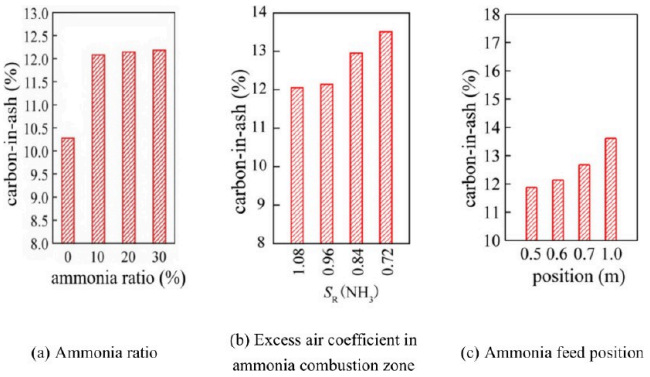
emission is relatively low, so it can be considered that the ammonia is completely burned in the boiler.[107,148]

As for the unburned carbon, due to the comparatively low temperature of NH_3 combustion, the unburnt carbon contained in fly ash initially declined before rising as the ammonia blending ratio increased in an 8.5 MW coal-fired boiler with eight swirl burners.[118] The lowest value of unburned carbon (about 3.6%) was obtained when NH_3 ratio was 10%. When NH_3 content reached 80%, unburned carbon would increase to 7%, which is higher than burning coal alone (4%).[118] When ammonia-doped ratio reached 20%, the carbon content in the fly ash increased by 20−60% compared to coal combustion.[9] Numerical simulations were performed by Ma et al.,[133] who found that as ammonia-doping ratio increased, if the excess air coefficient decreased in the combustion zone, carbon content of fly ash would increase (Figure 29). This phenomenon can be attributed to the competitive relationship between NH_3 and coal during combustion, which weakens char combustion.[133]



(a) Ammonia ratio (b) Excess air coefficient in ammonia combustion zone (c) Ammonia feed position

Figure 29. Variation trend of carbon-in-ash under ammonia-coal blending. This figure was reproduced with permission from ref 133. Copyright 2022 China Coal Research Institute.

Furthermore, using the one-dimensional flame furnace, Wang et al.[134] revealed that the probability of fuel slagging would decrease as ammonia blending ratio increased (Table 6). A 25% blend will slightly mitigate fuel slagging, and a blend ratio of 45% will enormously mitigate slagging. Additionally, the ash content decreased as ammonia doping ratio increased. It may be because of the reduction of coal and surface ash deposition. The injected NH_3 would improve the properties of coal ash and slag, and thereby enhancing the safety of the boiler. In addition, Chen et al.[119] found that when ammonia doping ratio increased from 0 to 50%, the amount of fly ash in flue gas decreased from 26.9 to 12.3 g/m^3, which could cut the negative abrasion impacts caused by high gas velocity.

In a nutshell, ammonia/coal co-firing can reduce the tendency for ash and slag accumulation. As for the unburned matters, it is important to choose the appropriate combustion organization and ammonia blending ratio. The formation of localized oxygen-enriched regions by wall inlet ammonia injection or air-staged method allows for more complete combustion of carbon and ammonia.[118,158] Enhancing pulverized coal particles mixing with air, which can be realized by increasing the jet velocity by using an ammonia injection gun,[158] can lead to a further reduction of unburned carbon content. The increase of ammonia proportion can increase the carbon content of fly ash, and an ammonia blending ratio around 20% is more appropriate.[133]

5.2.3. Emission of Other Gaseous Pollutants. Ammonia co-firing, reducing the input of carbon and enhancing the input of hydrogen, presents a promising strategy to mitigate carbon (CO and CO_2) emissions. And theoretically, ammonia co-firing can heighten the content of H_2O in flue gas.[4,23] To be more specific, in ammonia co-firing scenarios, the H_2O concentration in flue gas was calculated to be about 1.7 times higher than burning coal alone.[148] This would accelerate the WGS reaction ($CO + H_2O \rightarrow CO_2 + H_2$) and thereby further inhibit the formation of CO.[148]

The concentration of CO indicates the level of the incomplete combustion. Cui et al.[98] suggested that the CO concentration increased and then decreased with increasing exit heights above the flat flame burner (HAB) (5−100 mm). At HAB < 60 mm, the preferential reaction of ammonia with O_2 reduced the ambient oxygen concentration, resulting in incomplete combustion of a large amount of carbon. Thus, the maximum CO concentration 19773.05 mg/Nm^3 was taken at HAB = 60 mm and the coal concentration of 0.1. This value is much higher compared to that obtained by burning coal alone. The experiment of Wang et al.[152] in an air-staged one-dimensional down-fired furnace concluded that zero CO occurred at the exit of the boiler under 0−100% NH_3 co-firing ratios. However, in the reduction zone, the highest CO content was 58620 ppm, which was much higher than in pure coal combustion (43790 ppm). In air-staged combustion, the gasification of char with CO_2 and H_2O were found to be responsible for the observed high concentration of CO in the reduction zone.[159,160]

Likewise, through the CFD modeling of a 1000 MW coal-fired boiler, Ishihara et al.[107] suggested that CO and CO_2 emissions decreased nearly 75% when NH_3 co-combustion rate increased from 0 to 80%. Large-scale experiments were performed by Xu et al.[10] in a 600 MW coal-fired power plant and the outcomes showed that ammonia co-firing with coal could cut CO_2 emission by 24.08 tons per hour for each 5% rise in the blending rate.

As the co-firing ratio improved, not only the CO_2 and CO concentrations in the furnace gradually decreased (0.8 times and 0.7−0.9 times respectively, with 20% ammonia doping rate),[148,161] but also the release and decomposition of H_2S was

Table 6. One-Dimensional Furnace Temperature and Slag Type[134]

fuel	measuring point	first stage	second stage	third stage	fourth stage	fifth stage	sixth stage	SC
coal	flue gas temperature (°C)	1345	1270	1180	1108	1043	894	1.54
	slag type	fusion	fusion	fusion	cohesion	weak cohesion	attached ash	
25% NH_3	flue gas temperature (°C)	1354	1292	1190	1093	1010	906	1.51
	slag type	fusion	fusion	fusion	weak cohesion	attached ash	attached ash	
45% NH_3	flue gas temperature (°C)	1290	1245	1144	1040	972	875	0.93
	slag type	fusion	cohesion	cohesion	weak cohesion	attached ash	attached ash	

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inhibited.[152] When the ammonia co-firing rate changed from 0 to 100%, the maximum concentration of H_2S was 159 ppm in the reduction zone and decreased to 0 ppm in the staged combustion zone.[152] However, H_2S is no longer produced in the combustion zone, where sufficient oxygen is available, which is possibly due to the decomposition reactions of $H_2S + O \rightleftharpoons SO + H_2$ and $H_2S + O \rightleftharpoons SH + OH$.[152]

5.3. Efficiency of the Co-fired Systems. To further facilitate the industrialization of ammonia co-firing, it is also essential to pay close attention to its impact on energy losses and the combustion efficiency. According to the published literature, the temperature distribution and radiation behavior in the furnace are significant elements affecting the boiler efficiency.[1] Due to ammonia injection, the H content in the fuel increases, and the total amount of water and overall releasing rate of water rise.[4,23] Consequently, exhaust heat loss increases, lowering the boiler efficiency under co-firing conditions (about 89%) slightly compared with that of coal combustion (about 86%).[108] Chen et al.[67] demonstrated that ammonia co-firing can meliorate the combustion of ammonia and reduce the boiler efficiency due to increased unburned carbon. Numerical calculations of a 330 MW coal-fired boiler by Ding et al.[9] suggested that when lignite with a calorific value of 15.94 MJ/kg was used, the mixing ratio of ammonia was increased from 0 to 100% and the thermal efficiency of the boiler was increased from 92.5 to 93.3%. Besides, the thermal efficiency of the co-firing seemed related to the calorific value of coals. To be more specific, when the calorific value of the coal was lower than that of NH_3, the thermal efficiency of the boiler was found to increase as the doping rate rose due to the increase in effective heat and temperature in the boiler.[9]

Xu et al.[10] investigated the exergy efficiency of a 600 MW coal-fired power plant co-fired with NH_3. Two ammonia/coal co-firing methods (the identical adiabatic flame temperature (AFT) scenario, the identical excess air coefficient (EAC) scenario and five ammonia doping ratios (0, 5, 10, 15, and 20%) were token into consideration. It was demonstrated that increasing the ammonia co-firing ratio from 0 to 20% would bring about continuously increased exergy loss of the furnace [from 383.83 to 502.52 MW (AFT) and 407.72 MW (EAC)] but decreased exergy loss of heat exchangers [from 251 to 247.73 MW (AFT) and 243.72 MW (EAC)] and fans [from 0.83 to 0.64 MW (AFT) and 0.69 MW (EAC)]. Overall, the exergy efficiency of the whole boiler system decreased by only 0.55−0.60%. Exergy efficiency can be enhanced in many ways. For example, the injection of NH_3 at appropriate flow rates into the furnace with relatively low O_2 concentration and high NO_x concentration can help reduce the flue gas temperature and enhance the thermal efficiency of the boiler.[9] Combined with O_2 enrichment combustion and deep air-staging, 50% ammonia co-firing increased the overall exergy efficiency from 51.65 to 51.78% in a 600 MW utility boiler.[162] In addition, Aljundi[163] emphasized that the adjustment of the excessive air coefficient and temperature of the inlet gas was predominant in controlling the exergy loss, which may provide a good reference for reducing exergy loss in ammonia/coal co-firing.

6. CHALLENGES AND PERSPECTIVES

Ammonia, a promising carbon-free fuel, has substantial potential to reduce CO_2 emissions in the power generation sector. The world's major carbon dioxide emitters, such as Korea, Japan, and China, are making significant efforts in developing ammonia/coal co-combustion. Nevertheless, the massive emissions of NO_x from high-temperature scenarios pose a significant challenge when using NH_3 as a carbon-free fuel. Consequently, developing advanced low-NO_x combustion concepts is critical for the utilization of NH_3. Several new concepts have been reported to successfully minimize NO_x, including but not limited to the following: (a) Fuel-rich combustion: Reducing the amount of oxygen-containing radicals (e.g., O and OH) in the combustion zone can decrease NO_x emissions but increases the risk of NH_3 slip; (b) Air-staged combustion: Optimizing the input of primary air, secondary air, and overfire air to create separate lean and fuel-rich zones can reduce NO_x emissions; (c) Advanced swirling burners: Designing the spray aperture and spray angle to create recirculation zones enhances NO_x reduction; (d) NH_3 combustion with partial decomposition: Converting NH_3 to N_2 and H_2 enhances NH_3 combustion while reducing NO_x emissions; (e) MILD combustion: Combining preheating and dilution strategies contributes to NO_x reduction.

Despite these advancements, the mechanisms behind NO_x mitigation are not very fully understood, impeding the development of high-efficient NO_x reduction technologies. Advanced diagnostic techniques for measuring active and unstable radicals such as OH, HNO, and NH_x are urgently required to clarify these mechanisms in NH_3 combustion. Furthermore, a better understanding of the interaction mechanisms of NH_3 and coal, for example, (1) the effect of NH_3 on the release of coal-nitrogen; (2) the impact of coal on the conversion of NH_3-nitrogen during the co-combustion process is also crucial for its broad utilization. Isotope labeled experiments should be designed for ammonia/coal co-combustion to analyze the interaction mechanisms of NH_3 and coal, and to finally quantify the relative contribution of coal-nitrogen and NH_3-nitrogen in the conversion to NO_x. The tracking of NO_x formation would help develop novel and improved technologies for NH_3 and coal co-combustion.

In addition, the reaction kinetics associated with NO_x formation and reduction during ammonia/coal co-combustion is significant for advancing NO_x control techniques. Current models that combine mechanisms for different fuels, such as the Konnov mechanisms[164] and San Diego mechanisms[165] for NH_3 and the Hashimoto mechanisms[166] for coal, are inadequate due to the coupling effects observed in co-combustion as described in ref 167. Therefore, a more accurate kinetic model describing ammonia/coal co-combustion is urgently needed to reproduce the combustion and emission features, so as to innovatively optimize the combustor to reduce NO_x. Furthermore, a search of the reported literature indicates that most of the reported works on NH_3 combustion are mainly focused on NO_x and ignore N_2O, whose GWP is 300 times that of CO_2. A relatively small concentration of N_2O could be enough to produce a great GWP, making it an important issue. More efforts are still required to investigate the formation and conversion mechanisms of N_2O when using ammonia as a fuel.

7. CONCLUSION

In this work, we carried out a comprehensive review on the efforts that contributed to the understanding of ammonia co-firing in boilers, covering (1) technical and economic feasibility; (2) pollutant emission; (3) combustion dynamic behavior and (4) efficiency of the co-fired systems. The challenges and future prospects in the area of NH_3 and coal co-firing were discussed subsequently, aiming to provide

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theoretical support for future large-scale application of ammonia co-firing technology. The conclusions derived from this review are listed as follows:

(1) The results indicate that combustion techniques such as stage-combustion, swirling combustion, and MILD combustion could reduce NO_x emission, but even with those technologies the NO_x emission is generally higher than burning coal alone. Therefore, eco-friendly and credible combustion technologies for NH_3 are still needed.

(2) The analysis of the demonstration projects indicates that the use of ammonia/coal co-firing in boilers can achieve high power ratios (up to 40%), but the mechanisms behind unburned NH_3 and NO_x emissions need further analyses in order to further enlarge the co-firing ratio.

(3) NO_x is the most concerning pollutant in ammonia/coal co-firing among the available literature. However, evaluating the potential of ammonia/coal co-combustion technologies requires consideration of factors beyond NO_x emission, including NH_3 slip, thermal efficiency, equipment durability, and costs.

(4) Significant attention should be paid to other pollutants such as H_2S, N_2O, SO_2, fly ash, and nitrogen-containing PAH. For instance, fly ash and SO_2 cause physical abrasion and high temperature corrosion to the heating surface. The increase of water vapor under ammonia co-firing conditions has been found to change the acid dew point of the combustion flue gas, which may cause low temperature corrosion to the tail part of the heating surface.

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■ REFERENCES

(1) Xu, J.; Zhu, H.; Xu, Y.; Yu, D. Research progress and prospect of ammonia cofiring in utility coal-fired boiler. *J. Huazhong Univ. Sci. Technol., Nat. Sci. Ed.* **2022**, *50* (7), 55−65.

(2) International Energy Agency (IEA). *CO_2 Emissions in 2022*; IEA: Paris, France, 2023; https://www.iea.org/reports/co2-emissions-in-2022 (accessed June 20, 2024).

(3) Oh, S.; Park, C.; Oh, J.; Kim, S.; Kim, Y.; Choi, Y.; Kim, C. Combustion, emissions, and performance of natural gas-ammonia dual-fuel spark-ignited engine at full-load condition. *Energy* **2022**, *258*, 124837.

(4) Chen, L.; Fang, S.; Shen, J.; Wu, J.; Cong, J.; Xiang, K. Research progress in ammonia fuel for power generation. *J. Eng. Thermophys.* **2022**, *43* (8), 2212−2224.

(5) Ministry of Economy, Trade and Industry (METI). *Green Growth Strategy through Achieving Carbon Neutrality in 2050*; METI: Tokyo, Japan, 2021; https://warp.da.ndl.go.jp/info:ndljp/pid/11713225/www.meti.go.jp/policy/energy_environment/global_warming/ggs/pdf/green_honbun.pdf (accessed June 20, 2024).

(6) Zhang, D.; Li, D.; Xu, L. Effect of CaO and Ash on CO_2 Gasification Characteristics of Coal Char. *Contemp. Chem. Ind.* **2021**, *50* (10), 2408−2411.

(7) Oexmann, J.; Kather, A.; Linnenberg, S.; Liebenthal, U. Post-combustion CO_2 capture: chemical absorption processes in coal-fired steam power plants. *Greenhouse Gases* **2012**, *2* (2), 80−98.

(8) Kather, A.; Rafailidis, S.; Hermsdorf, C.; Klostermann, M.; Maschmann, A.; Mieske, K.; Oexmann, J.; Pfaff, I.; Rohloff, K.; Wilken, J. *Research and Development Needs for Clean Coal Deployment*; IEA Clean Coal Centre: London, U.K., 2008; https://www.osti.gov/etdeweb/biblio/21037109 (accessed July 1, 2024).

(9) Ding, X.; Li, W.; Ma, D. Discussion on coal-fired units coupled with ammonia fuel: combustion characteristics and economy. *Therm. Power Gener.* **2022**, *51* (8), 20−28.

(10) Xu, Y.; Wang, H.; Liu, X.; Zhu, J.; Xu, J.; Xu, M. Mitigating CO_2 emission in pulverized coal-fired power plant via co-firing ammonia: A simulation study of flue gas streams and exergy efficiency. *Energy Convers. Manage.* **2022**, *256*, 115328.

(11) The Adminstrative Centre for China's Agenda 21, Global CCS Institute, Tsinghua University. *China CCUS Annual Report 2023*; Global CCS Institute: Melbourne, Australia, 2023; https://www.globalccsinstitute.com/wp-content/uploads/2023/03/CCS-Progress-in-China-CN.pdf (accessed June 21, 2023).

(12) Zhang, Y.; Xie, Z.; Dong, Q.; Feng, M.; Li, Z.; Mei, X. Carbon Emission Study of Alternative Fuels Applied to Coal-Fired Power Plants. *Energy Environ.* **2024**, No. 2, 70−72.

(13) Lee, H.; Lee, M.-J. Recent Advances in Ammonia Combustion Technology in Thermal Power Generation System for Carbon Emission Reduction. *Energies* **2021**, *14* (18), 5604.

(14) Wang, Q.; Hu, Z.; Shao, W.; Wang, Z.; Liu, H.; Li, X.; Cui, D. The present situation, challenges, and prospects of the application of ammonia-coal co-firing technology in power plant boilers. *J. Energy Inst.* **2024**, *113*, 101531.

(15) Guangming Online. *Helping To Achieve Significant Carbon Emission Reduction China's Coal-Fired Boiler Mixed Ammonia Combustion Technology To Achieve New Breakthroughs*; Guangming Online: Beijing, China, 2022; https://m.gmw.cn/baijia/2022-01/26/35473585.html (accessed May 11, 2024).

(16) The Korea Herald. *S. Korea To Burn Hydrogen, Ammonia at Thermal Power Plants*; The Korea Herald: Seoul, Republic of Korea, 2021; https://www.koreaherald.com/view.php?ud=20211117000619 (accessed June 21, 2024).

(17) Tan, H.; Wang, X.; Yang, F.; Deng, S.; Ruan, R. Progress in low carbon technologies for large-scale coal-fired power plants. *J. China Coal Soc.* **2024**, *49* (2), 1052−1066.

(18) JERA. *Commencement of Joint Study on Ammonia Co-firing in Republic of the Philippines*; JERA: Tokyo, Japan, 2021; https://www.jera.co.jp/en/news/information/20230210_1084 (accessed May 11, 2024).

(19) New Energy and Industrial Technology Development Organization (NEDO). *Development of Technologies for Carbon Recycling and Next-Generation Thermal Power Generation*; NEDO: Kawasaki, Japan, 2024; https://www.nedo.go.jp/english/activities/activities_ZZJP_100115.html (accessed May 11, 2024).

(20) Adani Power. *Adani Power Sustainable Power Generation*; Adani Power: Ahmedabad, India, 2022; https://www.adanipower.com/newsroom/media-releases/Adani-Power-sustainable-power-generation (accessed May 13, 2024).

(21) Valera-Medina, A.; Xiao, H.; Owen-Jones, M.; David, W. I. F.; Bowen, P. J. Ammonia for power. *Prog. Energy Combust. Sci.* **2018**, *69*, 63−102.

(22) Chai, W. S.; Bao, Y.; Jin, P.; Tang, G.; Zhou, L. A review on ammonia, ammonia-hydrogen and ammonia-methane fuels. *Renewable Sustainable Energy Rev.* **2021**, *147* (39), 111254.

(23) Lyu, Q.; Wang, R.; Li, C.; Wang, C.; Du, Y.; Liu, Y. Research Progress on Co-firing Ammonia in Coal-fired Boiler. *Energy Conserv. Technol.* **2023**, *41* (4), 324−331.

(24) Hiraoka, K.; Fujimura, Y.; Watanabe, Y.; Kai, M.; Sakata, K.; Ishimoto, Y.; Mizuno, Y. Cost Evaluation Study on Low Carbon Ammonia and Coal Co-Fired Power Generation. *Proceedings of the NH_3 Fuel Conference*; Pittsburgh, PA, Oct 31−Nov 1, 2018.

(25) Cai, T.; Zhao, D.; Gutmark, E. Overview of fundamental kinetic mechanisms and emission mitigation in ammonia combustion. *Chem. Eng. J.* **2023**, *458*, 141391.

(26) Aziz, M.; Juangsa, F. B.; Irhamna, A. R.; Irsyad, A. R.; Hariana, H.; Darmawan, A. Ammonia utilization technology for thermal power generation: A review. *J. Energy Inst.* **2023**, *111*, 101365.

(27) Ma, S.; Yu, L.; Jiang, H.; Yang, P.; Li, Q.; Du, M.; Ma, J.; Zhu, H. Coal-Fired Power Plants Using Ammonia for Flexibility Enhancement under Carbon Control Strategies: Status, Development, and Perspectives. *Energy Fuels* **2024**, *38* (6), 4946−4965.

(28) Valera-Medina, A.; Vigueras-Zuniga, M. O.; Shi, H.; Mashruk, S.; Alnajideen, M.; Alnasif, A.; Davies, J.; Wang, Y.; Zhu, X.; Yang, W.; et al. Ammonia combustion in furnaces: A review. *Int. J. Hydrogen Energy* **2024**, *49* (8), 1597−1618.

(29) Occupational Safety and Health Administration (OSHA). *Ammonia Refrigeration*; OSHA: Washington, D.C., 2024; https://www.osha.gov/ammonia-refrigeration (accessed April 23, 2024).

(30) Crolius, S.; Pugh, D. G.; Morris, S.; Valera-Medina, A. Safety Aspects. In *Techno-Economic Challenges of Green Ammonia as an Energy Vector*; Academic Press: Cambridge, MA, 2021; Chapter 10, pp 221−257, DOI: 10.1016/B978-0-12-820560-0.00010-2.

(31) International Association of Classification Societies (IACS). *Control of Ammonia Releases in Ammonia Fuelled Vessels*; IACS: London, U.K., 2024; https://iacs.s3.af-south-1.amazonaws.com/wp-content/uploads/2024/01/17163429/UR-H1-New-Jan-2024.pdf (accessed 2024−06−21).

(32) Duan, L.; Li, T. Research progress of ammonia combustion characteristic and stable-combustion technology. *J. Huazhong Univ. Sci. Technol., Nat. Sci. Ed.* **2022**, *50* (07), 41−54.

(33) Kobayashi, H.; Hayakawa, A.; Somarathne, K. D. K. A.; Okafor, E. C. Science and technology of ammonia combustion. *Proc. Combust. Inst.* **2019**, *37* (1), 109−133.

(34) International Energy Network. *Synthesis of Ammonia Becomes a "Noah's Ark" of Hydrogen Energy*; International Energy Network:

https://doi.org/10.1021/acs.energyfuels.4c00872
Energy Fuels XXXX, XXX, XXX−XXX

Beijing, China, 2022; https://h2.in-en.com/html/h2-2412152.shtml (accessed April 22, 2024).
(35) Yapicioglu, A.; Dincer, I. A review on clean ammonia as a potential fuel for power generators. *Renewable Sustainable Energy Rev.* **2019**, *103*, 96−108.
(36) Miller, J. A.; Smooke, M. D.; Green, R. M.; Kee, R. J. Kinetic Modeling of the Oxidation of Ammonia in Flames. *Combust. Sci. Technol.* **1983**, *34* (1−6), 149−176.
(37) Guiberti, T. F.; Pezzella, G.; Hayakawa, A.; Sarathy, S. M. Mini Review of Ammonia for Power and Propulsion: Advances and Perspectives. *Energy Fuels* **2023**, *37* (19), 14538−14555.
(38) Zhu, X.; Du, J.; Yu, Z.; Cheng, Y.-B.; Wang, Y. NO_x Emission and Control in Ammonia Combustion: State-of-the-Art Review and Future Perspectives. *Energy Fuels* **2024**, *38* (1), 43−60.
(39) Zhu, X.; Guiberti, T. F.; Li, R.; Roberts, W. L. Numerical study of heat release rate markers in laminar premixed Ammonia-methane-air flames. *Fuel* **2022**, *318*, 123599.
(40) Berwal, P.; Kumar, S.; Khandelwal, B. A comprehensive review on synthesis, chemical kinetics, and practical application of ammonia as future fuel for combustion. *J. Energy Inst.* **2021**, *99*, 273−298.
(41) National Association of Regulatory Utility Commissioners (NARUC). *Coal and Carbon Management Guidebook: Coal-to-Hydrogen Opportunities and Challenges*; NARUC: Washington, D.C., 2021; https://pubs.naruc.org/pub/63211779-1866-DAAC-99FB-C7D38972AEB8 (accessed June 21, 2024).
(42) Chehade, G.; Dincer, I. Progress in green ammonia production as potential carbon-free fuel. *Fuel* **2021**, *299* (2), 120845.
(43) Worrell, E.; Price, L.; Neelis, M.; Galitsky, C.; Nan, Z. *World Best Practice Energy Intensity Values for Selected Industrial Sectors*; Lawrence Berkeley National Laboratory (LBNL): Berkeley, CA, 2007; LBNL-62806, DOI: 10.2172/927032.
(44) Lee, K.; Liu, X.; Vyawahare, P.; Sun, P.; Elgowainy, A.; Wang, M. Techno-economic performances and life cycle greenhouse gas emissions of various ammonia production pathways including conventional, carbon-capturing, nuclear-powered, and renewable production. *Green Chem.* **2022**, *24* (12), 4830−4844.
(45) Shi, J.; Zhu, Y.; Feng, Y.; Yang, J.; Xia, C. A prompt decarbonization pathway for shipping: Green hydrogen, ammonia, and methanol production and utilization in marine engines. *Atmosphere* **2023**, *14* (3), 584.
(46) Lee, B.; Lim, D.; Lee, H.; Lim, H. Which water electrolysis technology is appropriate?: Critical insights of potential water electrolysis for green ammonia production. *Renewable Sustainable Energy Rev.* **2021**, *143*, 110963.
(47) Fernandez, C. A.; Hatzell, M. C. Editors' choice-economic considerations for low-temperature electrochemical ammonia production: achieving Haber−Bosch parity. *J. Electrochem. Soc.* **2020**, *167* (14), 143504.
(48) Wang, M.; Khan, M. A.; Mohsin, I.; Wicks, J.; Ip, A. H.; Sumon, K. Z.; Dinh, C.-T.; Sargent, E. H.; Gates, I. D.; Kibria, M. G. Can sustainable ammonia synthesis pathways compete with fossil-fuel based Haber−Bosch processes? *Energy Environ. Sci.* **2021**, *14* (5), 2535−2548.
(49) Kandemir, T.; Schuster, M. E.; Senyshyn, A.; Behrens, M.; Schlögl, R. The Haber−Bosch Process Revisited: On the Real Structure and Stability of "Ammonia Iron" under Working Conditions. *Angew. Chem., Int. Ed.* **2013**, *52* (48), 12723−12726.
(50) Aziz, M.; Wijayanta, A. T.; Nandiyanto, A. B. D. Ammonia as Effective Hydrogen Storage: A Review on Production, Storage and Utilization. *Energies* **2020**, *13* (12), 3062.
(51) Topsoe. *Ammonfuel—An Industrial View of Ammonia as a Marine Fuel*; Topsoe: Kongens Lyngby, Denmark, 2020; https://www.topsoe.com/hubfs/DOWNLOADS/DOWNLOADS%20-%20White%20papers/Ammonfuel%20Report%20Version%2009.9%20August%203_update.pdf (accessed June 21, 2024).
(52) Rosinski, S.; Coleman, K. Opportunities and Challenges for Co-firing Ammonia in Coal-Fired Boilers. *Proceedings of the ASME Power Applied R&D 2023*; Long Beach, CA, Aug 6−8, 2023; POWER2023-107257, V001T01A001, DOI: 10.1115/POWER2023-107257.
(53) MacFarlane, D. R.; Cherepanov, P. V.; Choi, J.; Suryanto, B. H. R.; Hodgetts, R. Y.; Bakker, J. M.; Ferrero Vallana, F. M.; Simonov, A. N. A Roadmap to the Ammonia Economy. *Joule* **2020**, *4* (6), 1186−1205.
(54) Future Market Insights (FMI). *Green Ammonia Market*; FMI: Newark, DE, 2022; https://www.futuremarketinsights.com/reports/green-ammonia-market (accessed March 8, 2024).
(55) International Renewable Energy Agency (IRENA). *Innovation Outlook Renewable Ammonia*; IRENA: Abu Dhabi, United Arab Emirates, 2022; https://www.irena.org/publications/2022/May/Innovation-Outlook-Renewable-Ammonia (accessed June 21, 2024).
(56) Rouwenhorst, K. H. R.; Van der Ham, A. G. J.; Mul, G.; Kersten, S. R. A. Islanded ammonia power systems: Technology review & conceptual process design. *Renewable Sustainable Energy Rev.* **2019**, *114*, 109339.
(57) Wu, Q.; Shen, J.; Yu, L.; Chen, X.; Ai, Y.; Chen, J.; Xue, H. Analysis on the Hydrogen-Ammonia Storage and Transportation Technology and Economical Efficiency against the "Dual-Carbon" Background. *Pet. New Energy* **2022**, *34* (5), 27−33.
(58) Weixin. *Sector: Rise of Seaborne Ammonia Trade*; Weixin: Beijing, China, 2024; https://mp.weixin.qq.com/s/YaQoqHgvZPWDCEqdkhSaQg (accessed May 14, 2024).
(59) Hatfield, O. Review of Global Ammonia Supply. *Proceedings of the Ammonia Energy Conference 2020*; Virtual, Nov 16−20, 2020.
(60) Ammonia Energy Association (AEA). *MAN Energy Solutions: An Ammonia Engine for the Maritime Sector*; AEA: Ashburn, VA, 2019; https://ammoniaenergy.org/articles/man-energy-solutions-an-ammonia-engine-for-the-maritime-sector/ (accessed May 14, 2024).
(61) Lin, T.; Pengbo, Y.; Chaofei, N.; Feng, Y.; Liqian, Z.; Fuhua, D.; Yu, L.; Lilong, J. Research progress on "ammonia-hydrogen" green energy roadmap and storage & transportation technology of liquid ammonia. *Oil Gas Storage Transp.* **2022**, *41* (10), 1115−1129.
(62) Fertilizers Europe. *Guidance for Inspection of and Leak Detection in Liquid Ammonia Pipeline*; Fertilizers Europe: Brussels, Belgium, 2008; https://www.fertilizerseurope.com/wp-content/uploads/2019/08/Guidance_for_inspection_of_and_leak_detection_in_liquid_ammonia_pipelines_FINAL_01.pdf (accessed June 21, 2024).
(63) New Scientist. *Nitrogen Oxides in Car Exhaust Kill Tens of Thousands in UK*; New Scientist: London, U.K., 2015; https://www.newscientist.com/article/dn28245-nitrogen-oxide-is-not-so-harmless-and-could-damage-human-health/ (accessed Oct 20, 2023).
(64) Hayakawa, A.; Arakawa, Y.; Mimoto, R.; Somarathne, K. D. K. A.; Kudo, T.; Kobayashi, H. Experimental investigation of stabilization and emission characteristics of ammonia/air premixed flames in a swirl combustor. *Int. J. Hydrogen Energy* **2017**, *42* (19), 14010−14018.
(65) Lindstedt, R. P.; Lockwood, F. C.; Selim, M. A. Detailed Kinetic Modelling of Chemistry and Temperature Effects on Ammonia Oxidation. *Combust. Sci. Technol.* **1994**, *99* (4−6), 253−276.
(66) Ravishankara, A. R.; Daniel, J. S.; Portmann, R. W. Nitrous oxide (N_2O): The dominant ozone-depleting substance emitted in the 21st century. *Science* **2009**, *326* (5949), 123−125.
(67) Chen, P.; Hua, C.; Jiang, B.; Gu, M.; Ge, Z.; Zhang, M.; Luo, K.; Fan, J.; Wang, Y. Influence mechanism of ammonia mixing on NO formation characteristics of pulverized coal combustion and N oxidation in ammonia-N/coal-N. *Fuel* **2023**, *336*, 126813.
(68) Zhou, S.; Yang, W.; Cui, B.; Tan, H.; Wang, X.; Li, L.; Wang, X.; Wang, J. Experimental study and kinetic analysis on pollutant characteristics of ammonia combustion. *J. Huazhong Univ. Sci. Technol., Nat. Sci. Ed.* **2022**, *50* (7), 121−129.
(69) Chen, Y.; Zhang, B.; Su, Y.; Sui, C.; Zhang, J. Effect and mechanism of combustion enhancement and emission reduction for non-premixed pure ammonia combustion based on fuel preheating. *Fuel* **2022**, *308*, 122017.
(70) Miller, J. A.; Smooke, M. D.; Green, R. M.; Kee, R. J. Kinetic Modeling of the Oxidation of Ammonia in Flames. *Combust. Sci. Technol.* **1983**, *34* (1−6), 149−176.
(71) Sorrentino, G.; Sabia, P.; Bozza, P.; Ragucci, R.; de Joannon, M. Low-NO_x conversion of pure ammonia in a cyclonic burner under

https://doi.org/10.1021/acs.energyfuels.4c00872
Energy Fuels XXXX, XXX, XXX−XXX

locally diluted and preheated conditions. *Appl. Energy* **2019**, *254*, 113676.
(72) Shrestha, K. P.; Lhuillier, C.; Barbosa, A. A.; Brequigny, P.; Contino, F.; Mounaïm-Rousselle, C.; Seidel, L.; Mauss, F. An experimental and modeling study of ammonia with enriched oxygen content and ammonia/hydrogen laminar flame speed at elevated pressure and temperature. *Proc. Combust. Inst.* **2021**, *38* (2), 2163−2174.
(73) Mei, B.; Zhang, X.; Ma, S.; Cui, M.; Guo, H.; Cao, Z.; Li, Y. Experimental and kinetic modeling investigation on the laminar flame propagation of ammonia under oxygen enrichment and elevated pressure conditions. *Combust. Flame* **2019**, *210*, 236−246.
(74) Khateeb, A. A.; Guiberti, T. F.; Zhu, X.; Younes, M.; Jamal, A.; Roberts, W. L. Stability limits and exhaust NO performances of ammonia-methane-air swirl flames. *Exp. Therm. Fluid Sci.* **2020**, *114*, 110058.
(75) Xiao, H.; Valera-Medina, A.; Bowen, P.; Dooley, S. 3D Simulation of Ammonia Combustion in a Lean Premixed Swirl Burner. *Energy Procedia* **2017**, *142*, 1294−1299.
(76) Khateeb, A. A.; Guiberti, T. F.; Wang, G.; Boyette, W. R.; Younes, M.; Jamal, A.; Roberts, W. L. Stability limits and NO emissions of premixed swirl ammonia-air flames enriched with hydrogen or methane at elevated pressures. *Int. J. Hydrogen Energy* **2021**, *46* (21), 11969−11981.
(77) Somarathne, K. D. K. A.; Colson, S.; Hayakawa, A.; Kobayashi, H. Modelling of ammonia/air non-premixed turbulent swirling flames in a gas turbine-like combustor at various pressures. *Combust. Theory Model.* **2018**, *22* (5), 973−997.
(78) Okafor, E. C.; Somarathne, K. D. K. A.; Hayakawa, A.; Kudo, T.; Kurata, O.; Iki, N.; Kobayashi, H. Towards the development of an efficient low-NO_x ammonia combustor for a micro gas turbine. *Proc. Combust. Inst.* **2019**, *37* (4), 4597−4606.
(79) Pugh, D.; Runyon, J.; Bowen, P.; Giles, A.; Valera-Medina, A.; Marsh, R.; Goktepe, B.; Hewlett, S. An investigation of ammonia primary flame combustor concepts for emissions reduction with OH*, NH_2* and NH* chemiluminescence at elevated conditions. *Proc. Combust. Inst.* **2021**, *38* (4), 6451−6459.
(80) Kurata, O.; Iki, N.; Matsunuma, T.; Inoue, T.; Tsujimura, T.; Furutani, H.; Kobayashi, H.; Hayakawa, A. Performances and emission characteristics of NH_3-air and NH_3-CH_4-air combustion gas-turbine power generations. *Proc. Combust. Inst.* **2017**, *36* (3), 3351−3359.
(81) Terasaki, T.; Hayashi, S. The effects of fuel-air mixing on NO_x formation in non-premixed swirl burners. *Symp. (Int.) Combust., [Proc.]* **1996**, *26* (2), 2733−2739.
(82) Reddy, V. M.; Katoch, A.; Roberts, W. L.; Kumar, S. Experimental and numerical analysis for high intensity swirl based ultra-low emission flameless combustor operating with liquid fuels. *Proc. Combust. Inst.* **2015**, *35* (3), 3581−3589.
(83) Warnatz, J.; Maas, U.; Dibble, R. W. *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*; Springer: Berlin, Germany, 2001.
(84) Hayakawa, A.; Goto, T.; Mimoto, R.; Kudo, T.; Kobayashi, H. NO formation/reduction mechanisms of ammonia/air premixed flames at various equivalence ratios and pressures. *Mech. Eng. J.* **2015**, *2* (1), 14-00402.
(85) Tang, Y.; Xie, D.; Shi, B.; Wang, N.; Li, S. Flammability enhancement of swirling ammonia/air combustion using AC powered gliding arc discharges. *Fuel* **2022**, *313*, 122674.
(86) Faingold, G.; Lefkowitz, J. K. A numerical investigation of NH_3/O_2/He ignition limits in a non-thermal plasma. *Proc. Combust. Inst.* **2021**, *38* (4), 6661−6669.
(87) Somarathne, K. D. K. A.; Hatakeyama, S.; Hayakawa, A.; Kobayashi, H. Numerical study of a low emission gas turbine like combustor for turbulent ammonia/air premixed swirl flames with a secondary air injection at high pressure. *Int. J. Hydrogen Energy* **2017**, *42* (44), 27388−27399.
(88) Okafor, E. C.; Somarathne, K. D. K. A.; Ratthanan, R.; Hayakawa, A.; Kudo, T.; Kurata, O.; Iki, N.; Tsujimura, T.; Furutani, H.; Kobayashi, H. Control of NO_x and other emissions in micro gas turbine combustors fuelled with mixtures of methane and ammonia. *Combust. Flame* **2020**, *211*, 406−416.
(89) Li, Z.; Zhang, Y.; Zhang, H. Kinetics modeling of NO emission of oxygen-enriched and rich-lean-staged ammonia combustion under gas turbine conditions. *Fuel* **2024**, *355*, 129509.
(90) Kim, N.; Lee, M.; Park, J.; Park, J.; Lee, T. A Comparative Study of NO_x Emission Characteristics in a Fuel Staging and Air Staging Combustor Fueled with Partially Cracked Ammonia. *Energies* **2022**, *15* (24), 9617.
(91) Pugh, D.; Bowen, P.; Valera-Medina, A.; Giles, A.; Runyon, J.; Marsh, R. Influence of steam addition and elevated ambient conditions on NO_x reduction in a staged premixed swirling NH_3/H_2 flame. *Proc. Combust. Inst.* **2019**, *37* (4), 5401−5409.
(92) Lyon, R. K.; Hardy, J. E. Discovery and development of the thermal DeNO$_x$ process. *Ind. Eng. Chem. Fundam.* **1986**, *25* (1), 19−24.
(93) Li, J.; Huang, H.; Kobayashi, N.; Wang, C.; Yuan, H. Numerical study on laminar burning velocity and ignition delay time of ammonia flame with hydrogen addition. *Energy* **2017**, *126*, 796−809.
(94) Lee, J. H.; Kim, J. H.; Park, J. H.; Kwon, O. C. Studies on properties of laminar premixed hydrogen-added ammonia/air flames for hydrogen production. *Int. J. Hydrogen Energy* **2010**, *35* (3), 1054−1064.
(95) Han, X.; Wang, Z.; Costa, M.; Sun, Z.; He, Y.; Cen, K. Experimental and kinetic modeling study of laminar burning velocities of NH_3/air, NH_3/H_2/air, NH_3/CO/air and NH_3/CH_4/air premixed flames. *Combust. Flame* **2019**, *206*, 214−226.
(96) Dai, L.; Hashemi, H.; Glarborg, P.; Gersen, S.; Marshall, P.; Mokhov, A.; Levinsky, H. Ignition delay times of NH_3 /DME blends at high pressure and low DME fraction: RCM experiments and simulations. *Combust. Flame* **2021**, *227*, 120−134.
(97) Hong, D.; Yuan, L.; Wang, C.; Wang, H. Insight into the Competitive and Synergistic Effects during Coal/NH_3 Cofiring via Reactive Molecular Dynamics Simulations. *Energy Fuels* **2023**, *37* (4), 3071−3082.
(98) Cui, M. S.; Niu, F.; Ji, R. S.; Duan, L.; Zhang, X. Experimental Study on Flame Chemical Composition of Coal and Ammonia Gas-Solid Jet in Flat Flame Burner. *ACS Omega* **2024**, *9* (10), 11769−11779.
(99) Zhang, Z.; Zhao, Z.; Zha, X.; Li, X.; Luo, C.; Wu, F.; Zhang, L. Computational Study on Cocombustion Characteristics of Pulverized Coal Blending with NH_3 under Moderate or Intense Low-Oxygen Dilution Combustion Mode. *Energy Fuels* **2022**, *36* (20), 12750−12762.
(100) IHI. *IHI Launches Partnership with JERA Asia for Ammonia Utilization in Malaysian Thermal Power Plants To Expand the Ammonia Value Chain*; IHI: Tokyo, Japan, 2022; https://www.ihi.co.jp/en/all_news/2022/resources_energy_environment/1198069_3488.html (accessed May 13, 2024).
(101) Takamasa, I.; Hiroki, I.; Juwei, Z.; Sakiko, I.; Toshiyuki, S. New technology of the ammonia co-firing with pulverized coal to reduce the NO_x emission. *Proceedings of the 2019 AIChE Annual Meeting*, Orlando, FL, Nov 10−15, 2019.
(102) Tsukasa, Y. Test of the Co-firing of Ammonia and Coal at Mizushima Power Station. *J. Combust. Soc. Jpn.* **2019**, *61* (198), 309−312.
(103) IHI. *JERA and IHI To Start a Demonstration Project Related to Ammonia Co-firing at a Large-Scale Commercial Coal-Fired Power Plant*; IHI: Tokyo, Japan, 2021; https://www.ihi.co.jp/en/all_news/2021/resources_energy_environment/1197406_3360.html (accessed May 13, 2024).
(104) IHI. *JERA and IHI Start Small-Volume Utilization of Fuel Ammonia at Hekinan Thermal Power Station Unit 5*; IHI: Tokyo, Japan, 2021; https://www.ihi.co.jp/en/all_news/2021/resources_energy_environment/1197542_3360.html (accessed May 13, 2024).
(105) Weixin. *It Is a "Black" Technology, the First in the World!*; Weixin: Beijing, China, 2022; https://mp.weixin.qq.com/s/VfsBZa9lQn62TDoTJwg6sg (accessed June 27, 2024).

https://doi.org/10.1021/acs.energyfuels.4c00872
Energy Fuels XXXX, XXX, XXX−XXX

(106) Niu, T.; Zhang, W.; Liu, X.; Hu, D.; Wang, T.; Xie, Y.; Wang, H. Industrial-scale experimental investigation of ammonia-coal cofiring in coal-fired boiler. *Clean Coal Technol.* **2022**, *28* (3), 193−200.
(107) Ishihara, S.; Zhang, J.; Ito, T. Numerical calculation with detailed chemistry on ammonia co-firing in a coal-fired boiler: Effect of ammonia co-firing ratio on NO emissions. *Fuel* **2020**, *274*, 117742.
(108) Genichiro, N.; Hiroki, I.; Takamasa, I.; Emi, O.; Yoshitomo, O. Development of Co-firing Method of Pulverized Coal and Ammonia to Reduce Greenhouse Gas Emissions. *IHI Eng. Rev.* **2020**, *53* (1), 1−10.
(109) JERA. *JERA and IHI To Start a Demonstration Project Related to Ammonia Co-firing at a Large-Scale Commercial Coal-Fired Power Plant*; JERA: Tokyo, Japan, 2021; https://www.jera.co.jp/english/information/20210524_677 (accessed Oct 20, 2023).
(110) JERA. *Starts the World's First Demonstration Testing of Ammonia Used for Thermal Power Generation*; JERA: Tokyo, Japan, 2024; https://www.jera.co.jp/en/action/discover/040 (accessed May 13, 2024).
(111) IHI. *IHI and Partners Launching Ammonia Co-firing Technology Feasibility Assessments at Coal Power Stations in Malaysia with Partners and for Other Companies To Establish Local Carbon-Free Ammonia Supply Chain*; IHI: Tokyo, Japan, 2021; https://www.ihi.co.jp/en/all_news/2021/resources_energy_environment/1197552_3360.html (accessed May 13, 2024).
(112) IHI. *IHI and TNB Power Generation Partnership To Create Decarbonization Roadmap in Coal-Fired Power Stations in Malaysia*; IHI: Tokyo, Japan, 2023; https://www.ihi.co.jp/en/all_news/2023/resources_energy_environment/1199835_3523.html (accessed May 13, 2024).
(113) Ammonia Energy Association (AEA). *Trailing Ammonia-Coal Co-firing in India*; AEA: Ashburn, VA, 2022; https://ammoniaenergy.org/articles/trailing-ammonia-coal-co-firing-in-india/ (accessed May 13, 2024).
(114) Ministry of Trade, Industry and Energy (MOTIE). *To Advance to the World's No. 1 Hydrogen and Ammonia Power Generation Country*; MOTIE: Sejong, Republic of Korea, 2021; https://www.motie.go.kr/kor/article/ATCL3f49a5a8c/164964/view (accessed May 13, 2024).
(115) Ministry of Trade, Industry and Energy (MOTIE). *Hydrogen and Ammonia Power Generation Is Essential for Carbon Neutrality*; MOTIE: Sejong, Republic of Korea, 2023; https://www.motie.go.kr/kor/article/ATCL3f49a5a8c/167156/view (accessed May 13, 2024).
(116) Recharge. *South Korea Aims To Burn Millions of Tonnes of Clean Hydrogen and Ammonia for Giga-Scale Power Production*; Recharge: London, U.K., 2021; https://www.rechargenews.com/energy-transition/south-korea-aims-to-burn-millions-of-tonnes-of-clean-hydrogen-and-ammonia-for-giga-scale-power-production/2-1-1099333?zephr_sso_ott=6R3MSm (accessed May 11, 2024).
(117) Ministry of Trade, Industry and Energy (MOTIE). *Expanding Core Mineral Cooperation with Resource-Rich Vietnam!*; MOTIE: Sejong, Republic of Korea, 2022; https://www.motie.go.kr/kor/article/ATCL8764a1224/155118242/view (accessed May 13, 2024).
(118) Zhang, J.; Ito, T.; Ishii, H.; Ishihara, S.; Fujimori, T. Numerical investigation on ammonia co-firing in a pulverized coal combustion facility: Effect of ammonia co-firing ratio. *Fuel* **2020**, *267*, 117166.
(119) Chen, L.; Wang, C.; Wang, W. Effect of ammonia co-firing on heat transfer, safety, and economy of coal-fired boilers. *Fuel* **2023**, *334*, 126649.
(120) Hanaoka, R. Carbon-Neutral Thermal Power Generation Using Ammonia Combustion technology development and boiler design to expand use of ammonia. *IHI Eng. Rev.* **2022**, *55* (1), 1−4.
(121) JERA. *CO_2 Emissions Free Thermal Power Generation Captures the Interest of the World*; JERA: Tokyo, Japan, 2023; https://www.jera.co.jp/en/action/discover/004 (accessed June 27, 2024).
(122) Recharge. *Expensive and Very Dirty|BNEF Slams Japan's Plans To Burn Hydrogen-Derived Ammonia with Coal for Power Production*; Recharge: London, U.K., 2022; https://www.rechargenews.com/energy-transition/expensive-and-very-dirty-bnef-slams-japan-s-plans-to-burn-hydrogen-derived-ammonia-with-coal-for-power-production/2-1-1322538 (accessed June 27, 2024).
(123) Toshiro, F.; Toshiyuki, S. Ammonia Energy Value Chain for Carbon Neutrality from Production to Utilization. *IHI Eng. Rev.* **2022**, *55* (1), 1−5.
(124) JERA. *4.4 Trillion-Yen Company Driving the Energy Transition in Resource-Poor Japan*; JERA: Tokyo, Japan, 2023; https://www.jera.co.jp/en/action/discover/002 (accessed June 27, 2024).
(125) Li, C.; Li, Z.; Liu, P.; Zhao, G. Levelized cost calculation of electricity in ammonia-coal co-combustion unit using green ammonia. *J. Chin. Soc. Power Eng.* **2022**, *42* (11), 1042−1050.
(126) Sun, Y.; Li, Z.; Wang, Q.; Zhang, J.; Kong, H. Low carbon pathway and life cycle assessment of ammonia co-firing in coal power plants under the context of carbon neutrality. *Energy Convers. Manage.* **2023**, *296*, 117648.
(127) National Bureau of Statistics of China. *China Statistical Yearbook 2022*; National Bureau of Statistics of China: Beijing, China, 2022; https://www.stats.gov.cn/sj/ndsj/2022/indexeh.htm (accessed June 21, 2023).
(128) Bicer, Y.; Dincer, I.; Zamfirescu, C.; Vezina, G.; Raso, F. Comparative life cycle assessment of various ammonia production methods. *J. Cleaner Prod.* **2016**, *135*, 1379−1395.
(129) Lee, B. H.; Bae, Y. H.; Cho, S. H.; Kim, G. M.; Jeon, C. H. Comprehensive technical review for fundamental characteristics and application of NH_3 co-firing with coal. *Chem. Eng. J.* **2023**, *474*, 145587.
(130) Ishaq, H.; Crawford, C. Review of ammonia production and utilization: Enabling clean energy transition and net-zero climate targets. *Energy Convers. Manage.* **2024**, *300*, 117869.
(131) Armijo, J.; Philibert, C. Flexible production of green hydrogen and ammonia from variable solar and wind energy: Case study of Chile and Argentina. *Int. J. Hydrogen Energy* **2020**, *45* (3), 1541−1558.
(132) Tan, H.; Zhou, S.; Yang, W.; Cui, B.; Deng, S.; Wang, J.; Wang, X. Economic Analysis of Ammonia and Research Progress of Coal-Ammonia Co-firing. *Proc. CSEE* **2023**, *43* (1), 181−191.
(133) Ma, L.; Fang, Q.; Zhang, C.; Chen, G.; Wang, X. Combustion and NO formation characteristics of pulverized coal co-firing with ammonia in a deep-air staging condition. *Clean Coal Technol.* **2022**, *28* (3), 201−213.
(134) Wang, Z.; Jia, Z.; Zhao, C.; Xiao, Y.; Feng, S.; Chu, H. Effect of ammonia on the characteristics of coal combustion. *J. Energy Inst.* **2023**, *109*, 101275.
(135) Gong, Y. Study on the influence of coal ammonia mixed combustion method and ammonia mixing ratio on fuel emission characteristics. *Coal Qual. Technol.* **2023**, *38* (4), 46−52.
(136) Morlanés, N.; Katikaneni, S. P.; Paglieri, S. N.; Harale, A.; Solami, B.; Sarathy, S. M.; Gascon, J. A technological roadmap to the ammonia energy economy: Current state and missing technologies. *Chem. Eng. J.* **2021**, *408*, 127310.
(137) Xia, Y.; Hadi, K.; Hashimoto, G.; Hashimoto, N.; Fujita, O. Effect of ammonia/oxygen/nitrogen equivalence ratio on spherical turbulent flame propagation of pulverized coal/ammonia co-combustion. *Proc. Combust. Inst.* **2021**, *38* (3), 4043−4052.
(138) Hadi, K.; Ichimura, R.; Hashimoto, G.; Xia, Y.; Hashimoto, N.; Fujita, O. Effect of fuel ratio of coal on the turbulent flame speed of ammonia/coal particle cloud co-combustion at atmospheric pressure. *Proc. Combust. Inst.* **2021**, *38* (3), 4131−4139.
(139) Ma, P.; Huang, Q.; Wu, Z.; Lyu, J.; Li, S. Optical diagnostics on coal ignition and gas-phase combustion in co-firing ammonia with pulverized coal on a two-stage flat flame burner. *Proc. Combust. Inst.* **2023**, *39* (3), 3457−3466.
(140) Yu, W. Experimental Study on Ignition Characteristics of Pulverized Coal Jet. M.S. Thesis, Tsinghua University, Beijing, China, 2014.
(141) Wu, Z.; Huang, Q.; Ma, P.; Yang, Y.; Si, T.; Li, S. Characteristics of single-coal-particle ignition in ammonia-coal cofiring process. *Clean Coal Technol.* **2023**, *29* (10), 108−115.

https://doi.org/10.1021/acs.energyfuels.4c00872
Energy Fuels XXXX, XXX, XXX−XXX

(142) Takahashi, H.; Hashimoto, N.; Watanabe, H.; Kurose, R.; Fujita, O. Prediction of soot formation characteristics in a pulverized-coal combustion field by large eddy simulations with the TDP model. *Proc. Combust. Inst.* **2019**, *37* (3), 2883−2891.
(143) Chen, C.; Wang, Z.; Zhu, R.; Tan, J.; He, Y.; Cen, K. Co-firing characteristics and fuel-N transformation of ammonia/pulverized coal binary fuel. *Fuel* **2023**, *337*, 126857.
(144) Chen, P.; Gong, C.; Hua, C.; Gu, M.; Jiang, B.; Fan, J.; Wang, Y. Mechanism analysis of fuel-N oxidation during ammonia-coal co-combustion: Influence of H_2O. *Fuel* **2023**, *342*, 127747.
(145) Jeon, M.; Lee, E.; Kim, M.; Jegal, H.; Park, S.; Chi, J. H.; Baek, S.; Lee, J.; Keel, S. I. Nitric oxide (NO) and nitrous oxide (N_2O) emissions during selective non-catalytic reduction and selective catalytic reduction processes in a pulverized coal/ammonia co-fired boiler. *J. Environ. Chem. Eng.* **2023**, *11* (2), 109398.
(146) Fan, W.; Wu, X.; Guo, H.; Zhu, J.; Liu, P.; Chen, C.; Wang, Y. Experimental study on the impact of adding NH_3 on NO production in coal combustion and the effects of char, coal ash, and additives on NH_3 reducing NO under high temperature. *Energy* **2019**, *173*, 109−120.
(147) Chen, P.; Jiang, B.; Wang, H.; Gu, M.; Fang, Y.; Wang, P. Experimental and theoretical calculations study on heterogeneous reduction of NO by char/NH_3 in the reduction zone of ammonia co-firing with pulverized coal: Influence of mineral Fe. *Fuel* **2022**, *310*, 122374.
(148) Ishihara, S.; Zhang, J.; Ito, T. Numerical calculation with detailed chemistry of effect of ammonia co-firing on NO emissions in a coal-fired boiler. *Fuel* **2020**, *266*, 116924.
(149) Jiang, B.; Gu, M.; Chen, P.; Wang, P.; Hua, C.; Fan, J.; Wang, Y. Experimental Study on NO Formation Characteristics of Ammonia-coal Co-combustion. *Proc. CSEE* **2023**, *43* (17), 6746−6755.
(150) Brouwer, J.; Heap, M. P.; Pershing, D. W.; Smith, P. J. A model for prediction of selective noncatalytic reduction of nitrogen oxides by ammonia, urea, and cyanuric acid with mixing limitations in the presence of co. *Symp. (Int.) Combust., [Proc.]* **1996**, *26* (02), 2117−2124.
(151) Ding, X.; Li, W.; Liu, P.; Kang, Z. Numerical calculation on combustion process and NO transformation behavior in a coal-fired boiler blended ammonia: Effects of the injection position and blending ratio. *Int. J. Hydrogen Energy* **2023**, *48* (76), 29771−29785.
(152) Wang, X.; Fan, W.; Chen, J.; Feng, G.; Zhang, X. Experimental study and kinetic analysis of the impact of ammonia co-firing ratio on products formation characteristics in ammonia/coal co-firing process. *Fuel* **2022**, *329*, 125496.
(153) Chen, J. C.; Castagnoli, C.; Niksa, S. Coal devolatilization during rapid transient heating. 2. Secondary pyrolysis. *Energy Fuels* **1992**, *6* (3), 264−271.
(154) Glarborg, P.; Jensen, A. D.; Johnsson, J. E. Fuel nitrogen conversion in solid fuel fired systems. *Prog. Energy Combust. Sci.* **2003**, *29* (2), 89−113.
(155) Cao, H.; Sun, S.; Liu, Y.; Wall, T. F. Computational Fluid Dynamics Modeling of NO_x Reduction Mechanism in Oxy-Fuel Combustion. *Energy Fuels* **2010**, *24* (1), 131−135.
(156) Li, M. Simulation Study on NO_x Emission Characteristics of Pulverized Coal Oxy-fuel Combustion. M.S. Thesis, Dalian University of Technology, Dalian, China, 2018.
(157) Saha, M.; Chinnici, A.; Dally, B. B.; Medwell, P. R. Numerical Study of Pulverized Coal MILD Combustion in a Self-Recuperative Furnace. *Energy Fuels* **2015**, *29* (11), 7650−7669.
(158) Tamura, M.; Gotou, T.; Ishii, H.; Riechelmann, D. Experimental investigation of ammonia combustion in a bench scale 1.2 MW-thermal pulverised coal firing furnace. *Appl. Energy* **2020**, *277*, 115580.
(159) Fan, W.; Li, Y.; Guo, Q.; Chen, C.; Wang, Y. Coal-nitrogen release and NO_x evolution in the oxidant-staged combustion of coal. *Energy* **2017**, *125*, 417−426.
(160) Mackrory, A. J.; Tree, D. R. Measurement of nitrogen evolution in a staged oxy-combustion coal flame. *Fuel* **2012**, *93*, 298−304.
(161) Yuan, J. Y.; Wang, P. P.; Ruan, C. J.; Huang, X. Y. Study on Co-firing characteristics of NH_3 and coal in the main burning zone of the coal staged combustion. *J. Phys.: Conf. Ser.* **2022**, *2208* (1), 012016.
(162) Lyu, Q.; Wang, R.; Du, Y.; Liu, Y. Numerical study on coal/ammonia co-firing in a 600 MW utility boiler. *Int. J. Hydrogen Energy* **2023**, *48* (45), 17293−17310.
(163) Aljundi, I. H. Energy and exergy analysis of a steam power plant in Jordan. *Appl. Therm. Eng.* **2009**, *29* (2−3), 324−328.
(164) Konnov, A. A. Implementation of the NCN pathway of prompt-NO formation in the detailed reaction mechanism. *Combust. Flame* **2009**, *156* (11), 2093−2105.
(165) University of California, San Diego. *San Diego Mechanism: Chemical Kinetic Mechanisms for Combustion Applications, Mechanical and Aerospace Engineering (Combustion Research)*; University of California, San Diego: La Jolla, CA, 2024; http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html (accessed June 21, 2024).
(166) Hashemi, H.; Hansen, S.; Toftegaard, M. B.; Pedersen, K. H.; Jensen, A. D.; Dam-Johansen, K.; Glarborg, P. A Model for Nitrogen Chemistry in Oxy-Fuel Combustion of Pulverized Coal. *Energy Fuels* **2011**, *25* (10), 4280−4289.
(167) Liu, W.; Zhang, H.; Wang, K.; Hu, Y.; Fan, W. The effect of H_2 and NH_3 on the pyrolysis of coal model compounds based on reactive molecular dynamics simulation. *J. Anal. Appl. Pyrolysis* **2024**, *179*, 106501.

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