A Comprehensive Review of Ammonia Co-firing in Steam Turbine Power Plants: Challenges and Opportunities

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Abstract. Hydrogen is a clean energy carrier with abundant availability but requires appropriate storage methods due to its low volumetric density in gaseous form. Ammonia is a promising hydrogen carrier because of its high volumetric density, ease of long-term storage, and well-established production infrastructure. Additionally, ammonia can be synthesized using renewable energy sources. As a substitute for fossil fuels, ammonia offers the advantage of being a carbon-free fuel, making it highly suitable for decarbonization initiatives currently undertaken by governments worldwide. Ammonia is typically used as a fuel in a co-firing scheme, which combines it with other fuels. Co-firing ammonia with coal in power plants is a cost-effective solution, as it leverages existing infrastructure to reduce carbon emissions by decreasing coal usage without significant investment costs. However, while the performance of co-firing ammonia combustion is comparable to pure coal combustion, the increase in NOx emissions requires careful mitigation. Proven methods, such as air staging and secondary fuel injection, can reduce NOx emission levels in flue gas while maintaining combustion stability. In this paper, the terms ammonia and NH3 are used interchangeably.

Keywords: *Ammonia, Combustion, Low Carbon, Energy Carrier, NOx, Air-Staging*

1 Introduction

To carry out strategies in the energy transition, the condition of the electricity system with all its obstacles must be carefully considered by the Indonesian government. In the context of environmental preservation, steam turbine power plants have become scapegoats for the increase of carbon gasses in the atmosphere, which is the leading cause of climate change. However, from an economic point of view, steam turbine power plants have made great contributions to driving economic growth. The electricity consumption for industry and households in Indonesia was 111.280 GWh and 71.479 GWh respectively in 2020 [1], mostly from the steam turbine power plant. At the time, current renewable energy technology can only partially replace steam turbine power plant. Indeed, the trend towards the cost of new and renewable energy is decreasing, but in practice, it cannot be applied immediately. Due to its intermittent nature, which depends on changing weather, variable renewable energy is still at risk of disrupting the grid frequencies.

Received ________, Revised _________, Accepted for publication __________

In the immediate future, it is crucial to maximize the efficiency and functionality of current steam turbine power plants, capitalizing on their technological and economic viability within their operational lifespan. These plants have substantial potential to facilitate the ongoing energy transition due to their capacity and adaptability. Addressing and minimizing the detrimental impacts associated with these power plants remains imperative. The strategy that can be applied is co-firing, adding ammonia to primary energy to increase the renewable energy in the energy mix. In order to achieve the energy mix target of 100% of renewable energy by 2060, implementing co-firing is good initiation due to the fact that it does not require a large capital expense. The trials that have been carried out thus far show results that are technically feasible and do not interfere the reliability of the power plant. The total capacity of Steam turbine power plant that can be co-fired in Indonesia is up to 18,895 MW [1].

Research on co-firing ammonia is being carried out a lot, especially in Japan and China. The results of this research can be used as a reference for the development of NH_3 co-firing in steam turbine power plants in Indonesia. According to Qiang Lyu et al. [2], As the percentage of ammonia rises, carbon emissions fall linearly in proportion. However, co-firing ammonia also causes negative effects that need to be considered. Ammonia contains nitrogen in its compounds, so when it is burned, it will produce NO_x, which is quite dangerous if released into the environment. However, this paper will also explain several methods for reducing NO_x flue gas emissions from co-firing ammonia combustion.

In this review paper, the application of ammonia co-firing combustion within steam turbine power plants will be assessed in detail. The characteristics of ammonia as an energy carrier, existing methods for producing ammonia, and the potential for producing ammonia from renewable resources are outlined. The following section delves into the utilization of ammonia as a fuel, outlining its combustion traits and scrutinizing the emission of NO_x resulting from its combustion. Next, a comprehensive overview of ammonia co-firing has been provided, encompassing its combustion properties, the generation of carbon and NO_x in the flue gas, and initiatives aimed at improving the co-firing process. Ultimately, the conclusions drawn from the collective insights gathered throughout the paper are presented.

2 Reviews on Ammonia as Energy Carrier

2.1 Ammonia as Hydrogen Carrier

Hydrogen is projected to be a future alternative energy because it does not produce carbon gas emissions. Large amounts of hydrogen can be found in plants and water. Hydrogen is a simple element consisting of one proton and one electron [3]. However, hydrogen does not exist alone and is usually bound in water. Hydrogen is known for its renewability, non-toxic gas, flammability, and high efficiency; it is the most abundant substance in the world [4].

Hydrogen is a colourless gas but can be categorized into several colour codes, which refer to the technology or energy source for the production process. Green hydrogen is obtained by electrolysis of water using renewable energy sources. Grey hydrogen is obtained by a steam reforming process from methane (grey) without capturing CO_2. Blue hydrogen comes from fossil fuels but applies carbon capture storage technology. Brown hydrogen is obtained from coal gasification [5]. A complete explanation can be seen in Figure 1.

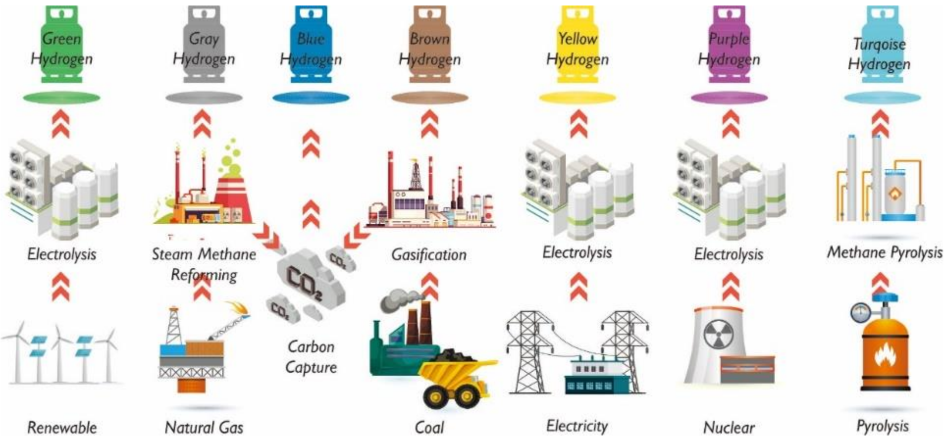

Figure 1 Hydrogen production method [5]

However, hydrogen has several drawbacks that could disrupt its application in the future. Hydrogen is volatile and can be dangerous. Storing hydrogen in gaseous form is also inefficient due to its low volumetric energy density [6]. Hydrogen is a gas at room temperature, and its volumetric density is small (0.0809 kgH_2/100L at 1 atm and 298 K) [7], so it is inefficient if stored and transported in gas form. A carrier method is needed to increase the H_2 gas density for transporting large amounts of hydrogen. Currently, there are three types of hydrogen energy carriers, namely ammonia, liquid H_2 and toluene-methylcyclohexane (MCH). Among them, ammonia has the most significant volumetric hydrogen density up to 1,69 times greater than liquid H_2 and 2,56 times greater than toluene-methylcyclohexane [8].

The volumetric energy density of ammonia contains twice the energy of liquid H_2, although the gravimetric energy density of ammonia is similar to liquid hydrogen. However, long-term ammonia storage is more feasible because it has a relatively high boiling point, namely 240 K at 0.1 Mpa [9]. According to the Hydrogen Economic Outlook, conversion costs from H_2 gas to ammonia are low compared with the liquefaction of hydrogen or hydrogen to MCH [10]. The energy required for the liquefaction process to make liquid hydrogen is 15 kWh/kg H_2 compared to 1.8-9.4 kWh/kg H2 energy used to produce ammonia [11]. Moreover, liquid H_2 has a lower combustion heat (8,58 Megajoule per liter) in contrast to ammonia (11,2 Megajoule per liter) [12]. Therefore, ammonia is attracting attention to be used as a hydrogen energy carrier. Ammonia can be used as an energy source that does not produce CO_2 during combustion. The table below provide specific parameters regarding the properties of NH_3.

Table 1 Properties of NH_3 [9]

Properties	**Unit**	**Value**
Molar mas	g/mol	17,03
Density at STP	kg/m^3	0,73
Heat capacity	J/mol.K	35,06
Boiling point	°C	-33,3
Critical temperature	°C	132,4
Critical pressure	Mpa	11,28
HHV	MJ/kg	22,5
LHV	MJ/kg	18,8
Auto-ignition temperature	°C	651
Flashpoint	°C	132

2.2 Ammonia Production

Ammonia is mainly produced for fertilizer, cleaning agents and explosives. With the increasing demand for ammonia in the energy industry, especially as an H_2 carrier, many ammonia production facilities are needed. In 2018 and 2019, total ammonia production worldwide was around 144 MT/year and 150 MT/year, respectively, and this year, it is predicted that 200 MT/y will be produced [13]. Like hydrogen, ammonia can also be produced in various ways and energy sources, including biomass, coal, natural gas, solar radiation, wind, geothermal, hydro and nuclear. Currently, most ammonia is produced from natural gas (CH_4), which reacts with steam, called steam reforming, which forms H_2, which reacts with N_2 extracted from the air [14]. However, ammonia can generally be produced in various ways, namely thermochemical, electrochemical, photochemical and plasma [15].

Image 2 indicates the most famous and conservative NH_3 synthesis process using natural gas, which was discovered by Fritz Haber and Carl Bosch a century ago by combining H_2 and N_2 [16]. Approximately 85% of total ammonia production worldwide uses this method [17].

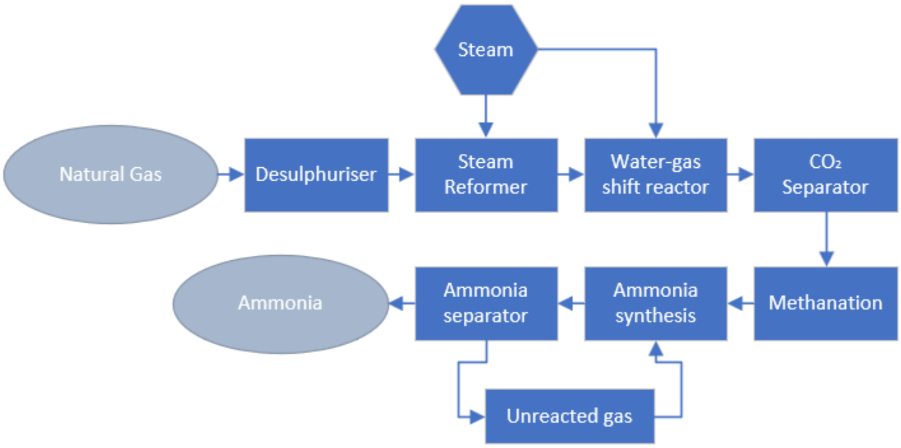

Figure 2 Haber-Bosch process of ammonia production [16]

The formation of ammonia compounds is an exothermic process and occurs spontaneously at low temperatures. Although this can occur at room temperature, the industrial scale's reaction speed needs to be higher. To obtain the desired production speed, high temperature and pressure are required. To produce ammonia effectively from its essential ingredients (nitrogen and hydrogen), the reaction is carried out with the help of an iron-based catalyst at relatively high temperatures and pressures, 400-500 °C and 10-30 Mpa, respectively. Energy is needed around 30 MJ/kg-NH_3 to reach this condition [18]. Due to the low conversion rate for a single pass (10-15% conversion of total reactant), the entire plant has several catalytic beds, so unreacted gases are fed to the next bed to increase the overall yield. The energy required will increase to 43 MJ/kg-NH_3 if H_2 is produced using electrolysis rather than steam reforming [12].

2.3 Green Ammonia

Ammonia production via Haber-Bosch technology has long been the main technology in ammonia production. However, this technology consumes a lot of energy and produces much CO_2. Using this method, producing one ton of ammonia releases 1.5 tons of CO_2 into the environment [19]. Fortunately, it is possible to capture CO2 and reduce it to urea and other useful products [6]. However, to synthesize green ammonia, several methods have been developed. Some of them are electrochemical, photocatalytic, biological, plasma-assisted and metallocomplexes supported syntheses, which are still classified as technology readiness level (TLR) of 1-3 [20]. Currently, technology has also been developed in the form of an electric HB process using green hydrogen as shown in Figure 3, and has a technology readiness level value of 3-9. Differing from conventional HB, which still uses steam reforming, HB electricity is supplied by green electricity [21].

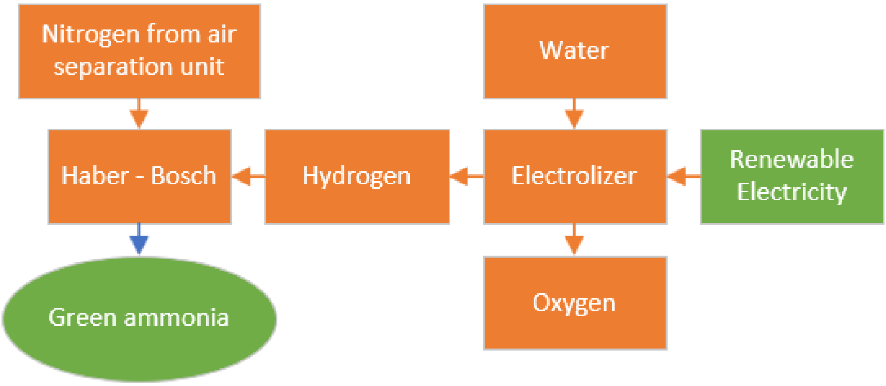

Figure 3 Production of ammonia from renewable sources [20]

2.4 Ammonia Storage System

At the atmospheric pressure, ammonia evaporates at a temperature of -33.3°C. Under standard temperature and pressure conditions, the volume of ammonia increases significantly up to 791 times greater than its volume in the liquid state[22]. Therefore, a method is required to store ammonia in its liquid state. There are three common methods for storing ammonia: pressure storage tanks, semi-refrigerated storage tanks, and fully refrigerated storage tanks [23]. Details regarding the operating pressure, capacity, and working temperature are provided in the table 2.

Table 2 Ammonia Storage Tank [23]

Storage Tank	Refrigerated Storage Tanks	Spheres	Pressure Storage (Bullets)
Storage Class	Fully Refrigerated	Semi Refrigerated	Unrefrigerated
Compressor	Two-stage	Single Stage	None
Temp. (°C)	-33 to -38	0 to 5	25 to 50
Pressure (kPa)	103 to 115	400 to 500	1800 to 2600
Capacity (ton)	3600 to 54500	450 to 3000	45 to 270

3 Reviews on Ammonia as Fuel

3.1 Ammonia Combustion in Coal Fired Power Plant

Ammonia combustion is an essential use for the future. The use of ammonia in boilers has been introduced recently, with up to 20% ammonia in co-firing combustion in steam turbine power plants. Meanwhile, Ishikawajima-Harima Heavy Industries Corporation succeeded in carrying out large-scale co-firing (20% of heat value) of ammonia in Hekinan Thermal Power Station Unit 5. Experiments were carried out at the Mizushima 155 MW power plant in 2017 by adding coal at a rate of 450 kg/h, equivalent to 0.6-0.8% of total fuel. Based on observations, there is no problem with the flue gas duct because ammonia dissociates at combustion temperatures. Meanwhile, the N component will not lead to fly ash adhesion, reduce the probability the particles to stick to the boiler walls. The results show that adding ammonia in this amount does not reduce the generator's efficiency [9].

Even though ammonia shows extraordinary potential as a renewable energy source, burning ammonia still has many shortcomings, such as weak combustion reactivity, low laminar burning velocity (LBV), and high NO_x emissions. The characteristics of ammonia that most significantly influence combustion are low LBV and ignition delay times, which can cause combustion imbalance and limit its direct application [24]. A possible solution is to use a fuel blending system such as ammonia-coal, which increases LBV and shortens the ignition delay time to obtain more stable combustion. On the other hand, emissions from NO_x and unburned ammonia are the main problems in ammonia combustion [25].

3.2 NO_x Formation

Emissions from burning ammonia in the form of NO_x and unburned ammonia are the main challenges in applying ammonia as a fuel. Nitrogen oxides pose a high risk to health and the environment. NO_x emissions can cause eutrophication and lung disease if inhaled. Under certain conditions, combustion can also produce nitrous oxide (N_2O), which has the potential as a global warming gas 280 times higher than CO_2. Unburned ammonia also affects the quality of combustion emissions [26]. The unburned ammonia content is influenced by the design of the combustor. Ammonia in flue gas will spearhead the formation of ammonium sulfides and nitrates, which can damage the environment [27].

In contrast to burning hydrocarbons, which produce NO_x at temperatures above 1800 K, in burning ammonia, the majority of NO_x is formed from direct nitrogen sources contained in ammonia [28]. The NO_x concentration is comparable to burning pure coal by modifying the location of the ammonia injection [29]. In theory, ammonia combustion only produces N_2 and H_2O vapor and does not produce NO_x. However, the complexity of kinetic reactions and combustion dynamics creates opportunities for NO_x formation [24].

4 Reviews on Ammonia Co Firing in Steam Turbine Power Plant

4.1 Recent Study on Ammonia Co-firing

Qiang Lyu et al. in 2022 [2] conducted an ammonia/coal co-firing simulation on a 600 MW capacity steam generator. In this study, a 3-dimensional numerical study on co-firing ammonia in large-scale boilers was carried out for the first time. Qiang Lyu investigated the influence of co-firing ratio, deep-air staging, and additional percentage of O_2 on the combustion process. This research shows that the combustion results are good for all case variations because the furnace temperature is relatively high, and the boiler is large-scale. Carbon emissions decrease linearly in proportion to the increase in ammonia percentage. Flue gas with low NO_x concentrations can also be achieved in ammonia co-firing with additional air injection. Nevertheless, flue gas temperature is declining with the increase in ammonia, which can impact heat radiation and coal combustion. The main reason that can cause this to happen is that, in theory, ammonia's flame temperature is lower than coal's. In the co-firing ammonia, the ammonia burns quickly after entering the furnace. The ammonia concentration in most areas is 10^{-6}, which indicates that almost all of the ammonia is completely burned in the boiler. The flue gas temperature is higher than the ignition point of ammonia, namely 924 K. In addition, the size of the boiler designed for burning coal is large enough for mixing and reaction between ammonia and oxidants. The addition of O_2 can increase the temperature level in co-firing ammonia. By adding 30% O_2 through secondary air, when the co-firing ratio reaches 50%, the flue gas temperature in the furnace is comparable to 100% coal combustion. However, NO concentration also shows an increasing trend as O_2 concentration increases.

4.2 Ammonia Co-firing Ratio Impact in Flue Gas Emission

The ammonia co-firing ratio shows the percentage of how much ammonia content is compared to the total mass of ammonia plus coal that enters the boiler in a co-firing scheme. According to Juwei Zhang et al. [30] the co-firing ratio significantly affects unburnt carbon in fly ash, NO_x and NH_3 emissions. At a co-firing ratio of 10 cal.%, which indicates intense combustion, unburnt carbon in fly ash shows a minimum value, and NO concentration at the furnace exit offers a maximum value. When the co-firing ratio increases above 10 cal.%, the NO concentration at the furnace exit decreases gradually due to the $DeNO_x$ effect of unreacted ammonia on the downstream side. However, even though a small concentration of ammonia appears at the furnace exit, at a co-firing ratio above 40 cal.%, ammonia emissions increase sharply, thus requiring caution in designing burners and furnaces in implementing high co-firing ratios on large-scale boilers.

The simulation results are validated by Joao Sousa et al. [31] with experimental data carried out for several different gas concentrations at several positions in the reactor. The results show that by increasing the percentage of ammonia, CO_2 emissions are reduced by 26% compared to burning pure coal. CO emissions are reduced while H_2O concentrations increase in flue gas because burning ammonia triggers CO to react with H_2O, causing a reduction in CO. Unburnt carbon decreases as the ammonia concentration increases due to the large amount of combustion air. NO emissions are still at the same level as the results of burning pure coal for an ammonia percentage of 10%. In contrast, for an ammonia percentage of 20%-80%, NO emissions are reduced by up to 40% due to the $DeNO_x$ effect and ammonia catalytic effect by reducing NO to the form of N_2 and H_2O. Slight concentrations of NH_3 emissions were found at ammonia concentrations of 10%-20%, whereas at 40% ammonia concentrations, the amount of unreacted NH_3 increased. Because NH_3 contains no carbon, its replacement in coal burning directly reduces CO_2 emissions by eliminating coal carbon, as shown by the coal volatiles combustion equation ($C_xH_yO_z + O_2 \rightarrow CO_2 + H_2O$). Furthermore, injecting NH3 into the flue gas is known to inhibit CO oxidation to CO_2 ($CO + 0.5O_2 \rightarrow CO_2$) [31]. CO_2 emissions were reduced by up to 26% at a 20% co-fire ratio compared to pure coal combustion, as shown in Figure 4.

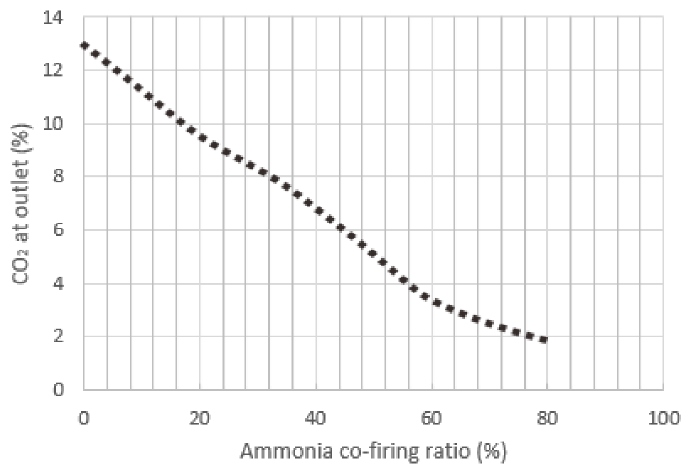

Figure 4 Effect of ammonia co-firing ratio on CO_2 emission [31]

4.3 Effect of Air Staging to Reduce NO_x Emission

As researched in several studies, air-staged combustion effectively reduces NO_x emission levels while ensuring combustion stability in the boiler furnace [32][33]. This method is the most frequently used method because of its effectiveness and economy. Air-staged combustion is research often carried out to reduce NO_x concentrations that can arise from co-firing ammonia in boilers. Research conducted by Wei Jin et al. [34] shows that increasing the secondary over fire ratio (SOFA) from 12% to 24% results in an 11% reduction in NO emissions. It was explained that this could happen because more air was being introduced through the SOFA installed on the burnout side, which reduced the combustion air supplied from the main burner and increased the reducing atmosphere in the primary combustion zone. On the other hand, when the SOFA ratio was reduced from 12% to 4%, NO emissions were reduced by about 16%. This can happen because reducing the SOFA ratio will encourage more air to pass through the primary combustion zone, creating better oxidation conditions, which encourage NO formation from ammonia oxidation. However, on the other hand, the more air that enters, the greater the cooling effect of the flue gas in the primary zone, which directly influences the combustion intensity. In general, NO transmission shows a decreasing trend when the SOFA ratio decreases drastically.

Xin Wang et al. [35] organized an combustion test on a 45 kW furnace to determine the effect of air-staged combustion on the formation of NOx in the case of ammonia co-firing. The research results show that the air-staging inlet's position significantly affects the co-firing ammonia product. The farther the distance between the air-staging inlet and the main burner, the lower the NO concentration produced at the flue gas outlet. However, if the distance between the air-staging inlet and the main burner is too far, it reduces combustion efficiency.

4.4 Secondary Fuel Injection Impact on NO_x Reduction

The addition of air-staging technology to co-firing ammonia combustion in boilers is the most commonly used method to reduce NOx levels. However, other efforts have been found to reduce NO_x content even though research discussing these technologies is still rare. One technology that can be applied is secondary fuel injection technology [36]. This technology is also known as re-burning technology [37], which is a process where hydrocarbon fuel is injected into the downstream side of the furnace to form a fuel-rich zone to convert NO_x into hydrogen cyanide (HCN). The re-burning fuel can be in the form of gas, liquid or solid phase with an amount of around 10-30% with a reduction level of 25-65%.

Sheng Su et al. [38] conducted experiments on a 36 kW furnace to determine the effect of gaseous re-burning on the combustion process. The experiment results show that 50% NO_x reduction and low carbon loss can be achieved when gaseous reburn fuel is 10-50% and the average excess air coefficient of re-burn zone is around 0.8-0.9. Meanwhile, based on experiments conducted by M Chernetskiy et al. [39], re-burning using standard dust-coal reduces NO_x by 37.5%. However, it increases heat loss in unburned carbon by 61%, mainly due to the non-optimal stoichiometric ratio. However, using mechanically-activated micronized coal as the material injected in re-burning technology will reduce NO_x levels by 49%, and heat loss is only 3.3% higher compared to the case without re-burning. The NO_x reduction rate increases with increasing reburn fuel fraction and reaches an optimal point of 15-20% [40]. Methane re-burning is also able to reduce NO_x levels in flue gas, with a re-burning percentage of 7.5-12.5% can reduce NO_x emissions from 7.02% to 25.61% [41].

5 Conclusion

Hydrogen is widely regarded as a clean and environmentally friendly energy carrier due to its lack of harmful carbon emissions and other pollutants. However, its low density at standard temperature and pressure presents significant challenges for storage and handling. Among various storage mechanisms, ammonia (NH3) offers notable advantages, particularly in terms of energy density, transport practicality, and usability. While the majority of NH_3 production currently relies on the conventional Haber-Bosch process, which generates high CO_2 emissions, advancements in technology suggest that mass production of green ammonia is becoming increasingly viable.

One widely explored application of ammonia is its direct combustion, which has gained attention as an effective method to reduce greenhouse gas emissions. In the context of achieving carbon reduction targets, ammonia co-firing in steam turbine power plants holds significant potential to decrease CO_2 emissions. By replacing a portion of coal, a major contributor to CO_2 emissions, with carbon-free ammonia, the amount of CO_2 in flue gas can be significantly reduced.

Despite its benefits, several challenges hinder the implementation of ammonia co-firing. One key issue is the presence of unburned ammonia in flue gas, which necessitates further research to design burners capable of achieving complete combustion. Additionally, ammonia co-firing generates higher concentrations of NOx compared to pure coal combustion, posing environmental and health risks. To address this, technologies such as air-staging and secondary fuel injection have been developed to reduce NO_x emissions without compromising combustion efficiency. Among these, air-staging technology is the most widely researched and offers an effective and practical solution.

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