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Impact of NH_3 Injection Location on NOx Emissions and Temperature Distribution in LPG-Based Cofiring Systems

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Abstract: Ammonia (NH_3) cofiring is a promising strategy to lowering the CO_2 emissions from fossil fuel combustion. Indonesia is currently pursuing green ammonia production using plentiful renewable resources like geothermal and hydropower. As the country aims to achieve net-zero emissions by 2060, incorporating green ammonia into existing thermal systems, particularly in the power and industrial sectors, provides a possible transition path. However, the potential for significant increases in NO_x emissions may hinder widespread NH_3 cofiring capture. This study investigates the effect of ammonia injection position on flame stability, combustion temperature, and NO_x emissions in a lab-scale co-firing system using LPG and ammonia, simulating partial ammonia substitution in industrial burners. Five axial injection positions were tested to assess the influence on emission characteristics and flame performance. The results show that downstream injection of ammonia significantly reduces NO_x emissions due to lower flame temperature and delayed ammonia oxidation, whereas upstream injection yields higher thermal output but increases NO_x formation. The findings of this study contribute to the development of low-emission co-firing strategies, supporting the feasibility of green ammonia as a scalable, clean fuel in Indonesia's decarbonization agenda.

Keywords: Ammonia; cofiring; combustion; emission; LPG

1. Introduction

Ammonia is considered a potential green fuel, due to its high energy density and production capacity from renewable sources. In recent years, research has concentrated on developing ammonia as a feasible substitute for existing fossil fuels in transportation and energy generation[1–5)]. With developments in technology and increasing concerns about climate change, ammonia has emerged as a possible solution for lowering greenhouse gas emissions and transitioning to a more sustainable energy system[6–9)]. Ammonia has several advantages, including its chemical stability, simplicity of storage and transportation, and compatibility with existing infrastructure. As governments and industries around the world commit to reducing their carbon footprint, In the future, demand for ammonia as a green fuel is expected to continue to increase[2)]. As a result, further research and investment in ammonia production and utilization are crucial to accelerating the transition to a cleaner, more environmentally friendly energy future. Currently ammonia with alkane mixture is being considered, with ammonia's carbon-free nature offering high energy density; higher than compressed air. Therefore ammonia is proposed for use in power generation[10–15)].

Analysis of three Indonesian ammonia production pathways from the perspective of technology, economy and environment is divided into gray, green and blue processes[16)]. Therefore, green ammonia will be based on renewable hydrogen[17–19)], blue ammonia will be based on carbon capture, and gray ammonia is based on natural gas. The findings show that while gray ammonia is the least expensive at $297/ton but has the highest emissions (2.73 tCO_2e/ton), blue ammonia produces significantly fewer emissions (0.28 tCO_2e/ton) at a minor cost increase ($390/ton). Even though green ammonia is nearly

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emission-free, it is still the most expensive ($696–1,024/ton) unless carbon prices rise and the cost of renewable electricity falls.

Another study uses the Life Cycle Assessment (LCA) to assess the environmental effects of ammonia production in Indonesia[20)]. The findings show that whereas CO_2 removal and power plant operations in the core process dominate GWP impacts, natural gas production and purification are the primary causes of abiotic depletion, toxicity, and carcinogenic impacts. GWP can be lowered by up to 43.3%, according to a sensitivity analysis[20,21)].

The most important factor in an ammonia combustion system is the position of ammonia injection as a green fuel source. The placement of ammonia injection points in the combustion process greatly affects the efficiency and emissions of the combustion process. While NO_x emissions also vary according to the injection position. According to research, when ammonia and pulverized coal are fired together, the position of the injection points is essential for reducing NO_x emissions[1,11,22–24)].

The correct position of the ammonia injector can optimize the mixing of air and fuel, resulting in more perfect combustion and less harmful pollutant emissions. The injection position can affect the performance and stability of the overall combustion system; Therefore, it is important to design and optimize the placement points of the ammonia injectors properly. For example, placing the injectors too close to the burner can result in uneven mixing and incomplete combustion, leading to higher emissions of NO_x. However, positioning the injectors too far away from the burner can result in inefficient mixing and use of ammonia, reducing its effectiveness as a clean fuel. Additionally, improper placement of the injectors can also result in increased maintenance costs and potential safety hazards due to the build-up of unburned ammonia. Therefore, it is crucial to consider not only the quantity of ammonia injected but also the precise location within the combustion system to ensure optimal performance and environmental benefits.

In this co-firing study, the effect of ammonia on liquefied petroleum gas consisting of n-butane and propane cannot be ignored. According to Miyazaki and Shida[25)], ammonia does not react with alkanes C_nH_{2n+1} and the possibility of electron transfer is very small. According to Mei. et.al,[26)], Modeling analysis was carried out to determine the balance of the mixture between NH_3 and air against the heating effect, with the result that thermal influences and plays a role in increasing the propagation of the NH_3 laminar flame in the partial fuel cracking strategy, while other factors that influence are pressure factors, while cracking in combustion changes NO to NO_x [26)]. Figure 1 compares the energy densities of various fuels[31)], including LPG and ammonia.

According Mathieu, et.al,[27)], NH_3 is known to be adsorbed on stainless steel, so the experimental set-up material needs to be considered. Several factors that affect the test include a wide temperature range (1560-2455 K), pressure (about 1.4, 11, and 30 atm) and balanced mixture ratio (0.5, 1.0, and 2.0) for a very dilute mixture of ammonia (98–99%)[27)]. The implications need to be pre-assessed before NH_3 co-firing technology is used widely in the future. Additionally, there are several technical problems while burning ammonia along with coal. Combustion experiments are among the earlier studies on ammonia–coal co-firing[3,28–30)] One area where further research is needed is the impact of varying injection positions on combustion efficiency and emissions reduction. While it is known that proper positioning of ammonia injectors is important, the specific effects of different placement strategies on combustion performance are not yet fully understood. This gap in knowledge presents an opportunity for future studies to explore the optimal placement of ammonia injectors in order to maximize the environmental benefits of co-firing with ammonia. By investigating the effects of injection position on combustion stability, emissions reduction, and overall system performance, researchers can provide valuable insights that will inform the design and operation of future co-firing systems.

2. Ammonia Combustion

Previous studies on ammonia injection in combustion systems have primarily focused on its impact on emissions reduction and combustion efficiency. Several studies have shown that ammonia injection can lead to significant reductions in nitrogen oxide emissions, as well as improvements in overall combustion efficiency. However, the optimal injection strategy for maximizing these benefits remains unclear. To date, research on the effect of injection position on combustion stability and system performance is still limited. This literature review will examine the existing research on ammonia injection in combustion systems and identify gaps in knowledge that warrant further investigation.

Theoretical background on ammonia-LPG cofiring and its

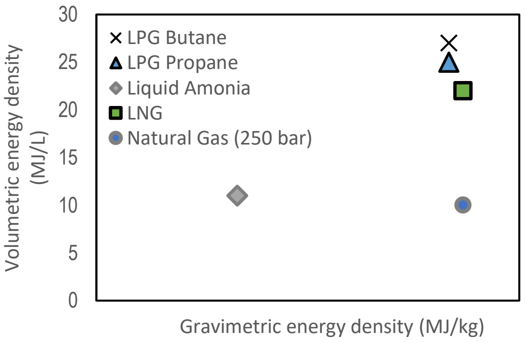


Fig. 1: Gravimetric and volumetric energy density of combustible materials

impact on emissions and combustion characteristics will be explored, with a focus on understanding the chemical reactions that take place during the combustion process. The potential benefits of ammonia-LPG cofiring, such as reduced greenhouse gas emissions and increased fuel flexibility, will also be discussed. Furthermore, the challenges and limitations of this technology will be addressed, including issues related to ammonia storage and transportation. From the literature reviews above, a comprehensive overview of the current status of research regarding the combustion of ammonia and LPG is provided. In terms of storage and transportation, energy density is important because ammonia has a lower energy density than LPG.

Complete combustion of ammonia can result in the primary formation of nitrogen and water, without any subsequent production of NO_x compounds. One major issue with ammonia combustion, though, is that NO_x emissions are really significant during actual combustion. In an effort to reduce nitrogen oxide (NO_x) emissions from combustion, a complex and sequential process is required to classify the mixture. The composition of NO_x mostly consists of thermal NO_x and fuel NO_x. Thermal nitrogen monoxide (NO) is typically generated by the process of nitrogen (N_2) oxidation at temperatures ranging up to 1800 K. The utilization of the NO_x mechanism is prevalent in the explanation of thermal nitrogen monoxide (NO) production. The thermal NO reactions encompass three significant pathways, namely N-N + O = N-O + N, N + O-O = N-O + O, and N + O-H = N-O + H. The initial reaction serves as a constraining factor for the reaction rate and often occurs at temperatures exceeding 1,800 K. Hence, the regulation of temperature serves as a viable approach for mitigating the generation of thermal nitrogen oxide (NO) emissions [12,32,33].

The reaction pathways of NH_3 oxidation, to NO_x formation, and De-NO_x are depicted in Figure 2. The decomposition of ammonia to NH_2 occurs through the H separation reaction with H/O/OH radicals, as determined for all equivalent compound ratios. The capture of NH_2 and other secondary and tertiary NH is influenced by the equivalent compound ratio, temperature, and pressure. NO_x production increases as temperature decreases and equivalence ratios decrease through O-OH reactions via the H_2NO, H-NO pathways (upper half of the plot). While the reactions with H-NHi and through the N_2Hi pathway are driven at medium and high temperatures with rich equivalence ratios, the De-NO_x pathway in the lower half of the plot[16].

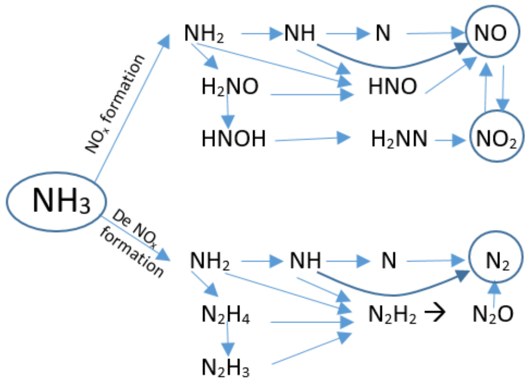


Fig. 2: NO_x formation and De-NO_x pathways

3. Material and Methods

3.1. Material

The use of ammonia as a co-firing fuel as an alternative fuel that replaces several fossil fuels is a solution that needs to be taken to reduce carbon emissions in power plants. In the use of ammonia as a fuel, there are several things that need to be considered, including low flame stability, low combustion efficiency, and high NO_x emissions. Ammonia (NH_3) is a carbon-free chemical compound, a colorless and odorless gas. Pure ammonia is easily soluble in water and is hygroscopic and corrosive. However, ammonia is corrosive, the following explanation of the characteristics of ammonia is presented in Table 1.

One significant area of investigation involves the interaction between ammonia and other fuels, particularly in co-firing scenarios. Many studies have shown that the combustion of ammonia mixture with LPG is influenced by the position of ammonia injection, which alters the local combustion temperature and flame structure, which ultimately affects emissions such as NO_x and unburned hydrocarbons. According to Zhu et al., the entry of ammonia together with coal into the combustion system will cause complex dynamics in the ignition of volatile fires, resulting in the formation of particulates, suggesting that injection strategies may be modified to optimize these parameters for better performance and lower emissions.

Table 1: Ammonia and LPG analysis[2,34,35]

Properties	Unit	Ammonia	LPG
Formula	-	NH_3	C_3H_8– C_4H_{10}
LHV	MJ/kg	18.8	45.7
Flammability limits, gas in air	Vol, %	16.25	1.81-8.86
Flame speed	m/s	0.15	0.83
Auto Ignition temp.	°C	651	470
Flash point	°C	-33.4	-87.7
Min. ignition energy	MJ	8	n.a
Fuel density	kg/m^3	602.8	1,898
Energy density	MJ/m^3	11,333	86,487
Latent heat vap.	kJ/kg	1,369	44.4
Storage method	-	Comp. liq	Comp. liq
Storage temp.	°C	25	25
Storage pressure	kPa	1030	850

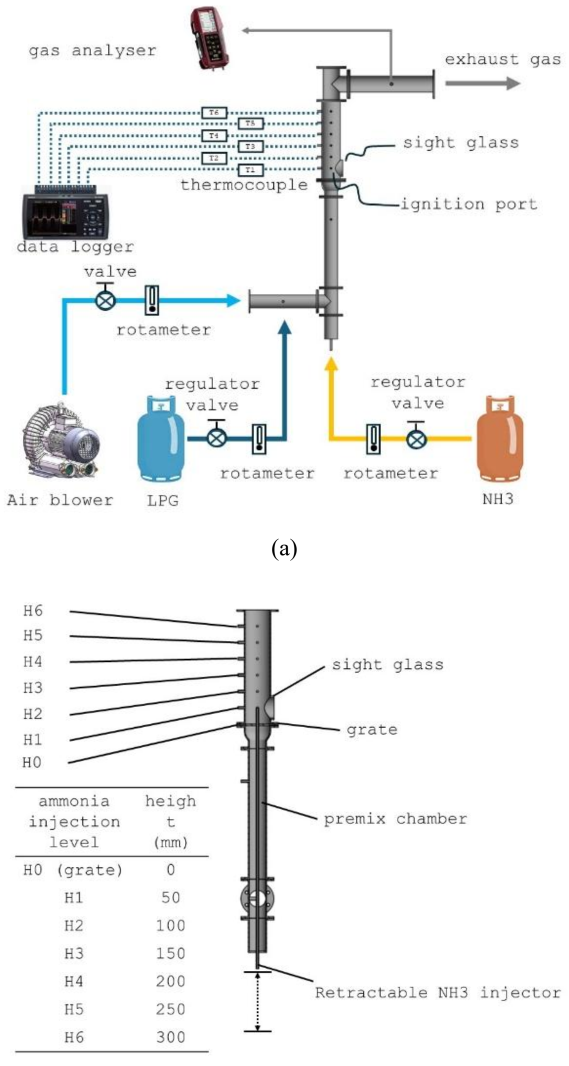
Several adjustments were made to reduce the increase in NO$_x$ emissions commonly associated with the use of ammonia in power plants

3.2. Experimental setup

This study used a cofiring simulator furnace with a capacity of 25 kW. Figure 3 shows the schematic diagram and ammonia injection system in the combustion chamber. The simulator furnace is constructed of 304 stainless steel tubing, with air and LPG inlet pipes having an inner diameter of 2 inches. The combined air with LPG is combined before being burned in a combustion chamber with an inner diameter of 3 inches and a height of 40 centimeters. The combustion chamber contains two peephole glasses that monitor the ignition of LPG and ammonia gas. This combustion chamber additionally features six height levels (H_1 - H_6) that are intended to identify the height position for injecting ammonia. Ammonia is injected using a stainless steel injected pipe with an inner diameter of ¼ in, which penetrates the grate of the combustion chamber, and the injection position can be adjusted by raising and lowering the pipe. A mechanical seal is installed between the ammonia pipe and the combustion chamber grate to prevent leakage. Thermocouples are installed at each ammonia height level (T_1 - T_6) to monitor the temperature distribution. Flue gas from the combustion chamber is directed to the adjuster pipe and monitored for flue gas emissions using a gas analyzer (MRU Optima 7).

This research is divided into two testing activities, namely LPG combustion testing and LPG and ammonia gas cofiring combustion testing. Combustion with LPG aims to determine the combustion characteristics in the simulator furnace and also as the base load of the cofiring test later.

The LPG combustion process begins by turning on the air blower for air supply into the simulator furnace and continues by flowing 5 liters per minute (lpm) of LPG into the furnace until premixed. The torch is lit in the combustion chamber to burn the LPG gas. The air blower is set so that the amount of excess oxygen in the flue gas is 2%. The flame occurs at the bottom of the combustion chamber at level 0 and expands with a peak temperature at H_3. The heat of combustion fills the combustion chamber and is maintained at temperatures of 850 – 875 °C. The temperature of each height H_1-H_6 is measured sequentially using thermocouples T_1-T_6. Meanwhile, the flue gas was measured using a gas analyzer. Ammonia injection starts from the highest injection height (H_6) to the lowest injection height (H_1). Ammonia injection was set at a flow rate of 0.6 lpm for each LPG gas rate. Temperature distribution was recorded by a thermo logger while exhaust emissions were measured using a gas analyzer. Ammonia injection at one test point was carried out for approximately 5 - 15 minutes.



(a)

ammonia injection level	height (mm)
H0 (grate)	0
H1	50
H2	100
H3	150
H4	200
H5	250
H6	300

(b)

Fig. 3: (a) Experimental set-up (b) Combustion chamber and NH_3 injection system

4. Results and discussion

The variation test procedure was carried out successively, beginning with full LPG and progressing to LPG-ammonia at level 1. Figure 4 shows temperature distribution in combustion chamber during LPG and co-firing Ammonia. Under full LPG combustion circumstances, the T_3 reached the highest temperature of 880 °C, followed by T_4 at 775 °C and T_2 at 735 °C. Throughout the whole LPG combustion process, temperature conditions are rather steady. The temperature distribution of T_3 at 835 °C, T_4 at 764 °C, and T_2 at 695 °C began to drop in the variation test with NH_3 injected at level 5, but T_5, T_1, and T_6 remained generally steady. Furthermore, temperatures of T_3 at 846 °C, T_4 at 773 °C, and T_2 at 700 °C increased slightly in the injection variation at level 4, though not as much as under full LPG settings. Although the injection variation at level 3 initially observed a fall in temperature, it gradually increased in temperature, much better than previously. At level 2 injection, the T_3 temperature drops to 860 °C, while the T_4 temperature rises to 815 °C. The T_2 temperature, on the other hand, decreased and even exceeded the T_5 temperature of 735 °C. In the injection variation at level 1, practically the entire temperature distribution declines, beginning with T_3, T_4, T_2, T_5, T_1, and T_6, and ignition conditions begin to be disrupted because the supply of O_2 concentration is very low and CO levels rise dramatically. According to the data in Table 1, ammonia has a lower heating value than LPG, a comparatively moderate burning velocity, and a limited flammability limit range when injected at the lowest amount. Injected ammonia at level 1 causes an unstable flame condition due to temperatures below 650^{o}C, which is below the auto-ignition point of ammonia. Because ammonia can oxide with air and is sustained in an environment temperature that is above its auto ignition temperature, the temperature distribution at and above levels 2, 3, and 4 increases relatively while injected at those concentrations and above.

In this experiment, ammonia injections were varied at five different levels with a fixed equivalent ratio. Excess oxygen conditions are near to zero for injection levels 1 and 2, with an equivalent ratio of roughly 1, as seen in Figure 5. The emission gas profile during the combustion test is shown in Figure 6. Ammonia in the equivalent ratio of low-quality fuel has substantial O and OH radical bonds, which promote the conversion of NH to NO. The fuel-NO_x production rate for oxidation mostly involves HNO and H_2NO compounds, as shown in Table 1, or the reaction of NH_2, NH, and N radicals with O_2, O, OH, and HO_2 to produce NO compounds. Some of the main reactions that form HNO are explained in the following reactions:

$$NH_2 + O = HNO + H \tag{1}$$

Reaction for de-NO_x, according Lyon et, all[37)], analyzed that at a temperature of 900-1100◦C, the O_2 compound in the oxidation reaction by reducing NO_x can be increased by using ammonia in a process called thermal De-NO_x. The De-NO_x Rate Pathway occurs in the oxidation of ammonia, with a rich equivalence ratio through the formation of NH_2; NH reacts with NO and NO_2 to form N-NH and N_2O to produce N_2. The De-NO_x reaction includes the following reactions[31,32)]:

$$NH_2 + NO = NNH + OH \tag{2}$$

$$NH_2 + NO = N_2 + H_2O \tag{3}$$

$$NH_2 + NO_2 = NO + H_2NO \tag{4}$$

$$NH_2 + NO_2 = N_2O + H_2O \tag{5}$$

$$NH + NO = N_2O + H \tag{6}$$

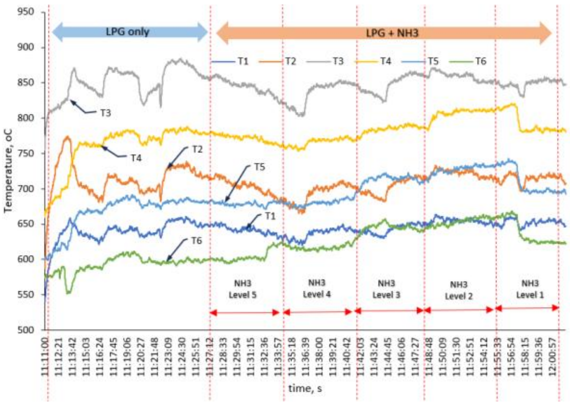


Fig. 4: Temperature distribution in combustion chamber during LPG and co-firing Ammonia

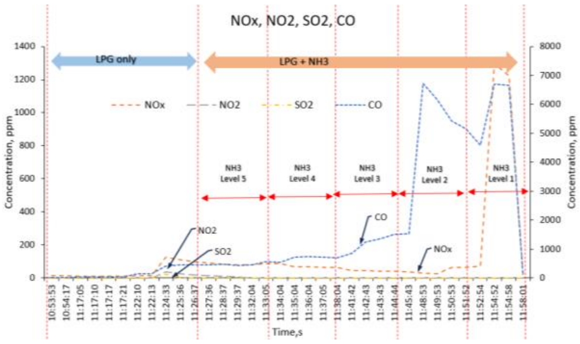


Fig. 5: Emission gas concentration at the discharge of combustion chamber during LPG and co-firing Ammonia

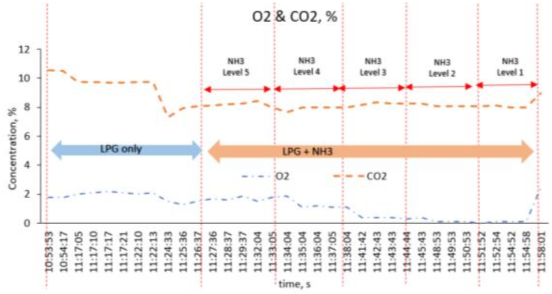


Fig. 6: O_2 and CO_2 gas at the discharge of combustion chamber during LPG and co-firing Ammonia

$$NH + NO = N_2 + OH \tag{7}$$

Meanwhile, injection levels 4 and 5 exhibit fuel-lean combustion resulting in low NO_x and CO emissions with an equivalent ratio of 0.3, but the gas leaving the furnace T_6 is only 615 ^{o}C. Meanwhile, level 3 with an equivalent ratio of 1.5 has low NO_x emissions and a maximum furnace exit temperature of 656 ^{o}C, but it also has an increase in CO emissions. Based on the use of ammonia fuel, the injection location with an equivalent ratio of 1.5 is the most optimal, resulting in the greatest increase in furnace exit gas temperature and the lowest NO_x emissions. Additional air injection through staging combustion is required to reduce the increase in CO emissions[36,38)], as seen in Figure 3.

5. Conclusion

Ammonia is commonly utilized in combustion furnaces to minimize NO_X emissions. The combustion strategy suggested in this study involves burning 100% LPG first, followed by NH_3 injection. Five positional variations can be seen at the point in time when the NH_3 injection position contributes as fuel, increasing the furnace temperature profile.

The results indicate that NO_x emissions rise when NH_3 is injected with an LPG burner in the same position, and then fall as the distance from the burner increases. When NH_3 was fed into the LPG flame zone or level 3 of the furnace, the NO_x level dropped. This suggests that the NO_x reduction of NH_3 cofiring is effectively achieved by the NH_3 injection site. In the flame zone, an equivalent ratio of 1.5 results in low NO_x emissions and a maximum furnace exit temperature of 656 °C, but it significantly increases CO emissions. However, using a staged combustion technique can lower CO emissions in NH_3 injection.

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