frontiers
in Energy Research

REVIEW
published: 06 October 2021
doi: 10.3389/fenrg.2021.760356

A Review on Combustion Characteristics of Ammonia as a Carbon-Free Fuel

Jun Li[1,2,3,4], *Shini Lai*[1,4], *Danan Chen*[1,4], *Rongjun Wu*[5], *Noriyuki Kobayashi*[5], *Lisheng Deng*[1,2,3] *and Hongyu Huang*[1,2,3,4]*

[1]Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, China, [2]Guangdong Key Laboratory of New and Renewable Energy Research and Development, Guangzhou, China, [3]Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou, China, [4]School of Energy Science and Engineering, University of Science and Technology of China, Guangzhou, China, [5]Department of Chemical Systems Engineering, Nagoya University, Nagoya, Japan

A comprehensive review of combustion characteristics of ammonia (NH_3) as a carbon free fuel is presented. NH_3 is an attractive alternative fuel candidate to reduce the consumption of fossil fuel and the emission of CO_2, soot, and hydrocarbon pollutants, due to its comparable combustion properties, productivities from renewable sources, and storage and transportation by current commercial infrastructure. However, the combustion properties of NH_3 are quite different from conventional hydrocarbon fuels, which highlight the specific difficulties during the application of NH_3. Therefore, this paper presents comparative experimental and numerical studies of the application of NH_3 as a fuel during combustion process, including the combustion properties of laminar burning velocity, flame structures, pollutant emissions for the application of NH_3 as a carbon free fuel. This paper presents the burning velocity and pollutant emissions of NH_3 alone and mixtures with other fuels to improve the combustion properties. The aim of this paper is to review and describe the suitability of NH_3 as a fuel, including the combustion and emission characteristics of NH_3 during its combustion process.

Keywords: ammonia, combustion characteristics, laminar burning velocity, pollutant emissions, carbon-free fuel

OPEN ACCESS

Edited by:
Xuezhong He,
Guangdong Technion-Israel Institute of Technology (GTIIT), China

Reviewed by:
Zhongde Dai,
Sichuan University, China
Guo-xiu Li,
Beijing Jiaotong University, China

***Correspondence:**
Hongyu Huang
huaghy@ms.giec.ac.cn

Specialty section:
This article was submitted to Advanced Clean Fuel Technologies, a section of the journal Frontiers in Energy Research

Received: *18 August 2021*
Accepted: *20 September 2021*
Published: *06 October 2021*

Citation:
Li J, Lai S, Chen D, Wu R, Kobayashi N, Deng L and Huang H (2021) A Review on Combustion Characteristics of Ammonia as a Carbon-Free Fuel. Front. Energy Res. 9:760356. doi: 10.3389/fenrg.2021.760356

INTRODUCTION

With the rapid economic development and population explosion of recent decades, the global primary energy consumption has increased dramatically. Coal, petroleum, and natural gas remain the major sources of energy across the world. Pollutants such as CO_2, CO, SO_2, NO_x, volatile organic compounds, particulate matter et al., are released by the combustion of petroleum, coal, and natural gas fuels (IEA, 2021). CO_2 is the major contributor to global warming. In the recent years, the development of new technologies aiming to reduce problems related to energy consumption, for application in both developed and developing countries, has become urgent, because of the increasing strictness of governmental regulation of energy and CO_2 emissions. Such developments lead to the search for carbon-free fuels, and the increasing importance of renewable energy sources (Astbury, 2008).

Combustion process during various industry processes contributed huge amount of CO_2 emissions. In order to obtain the target of zero-carbon emissions, it is necessary to reduce CO_2 emissions with the application of carbon-free fuel in combustion system. NH_3 is an attractive hydrogen carrier with a high hydrogen density of 17.8% per unit weight, which can be considered as a

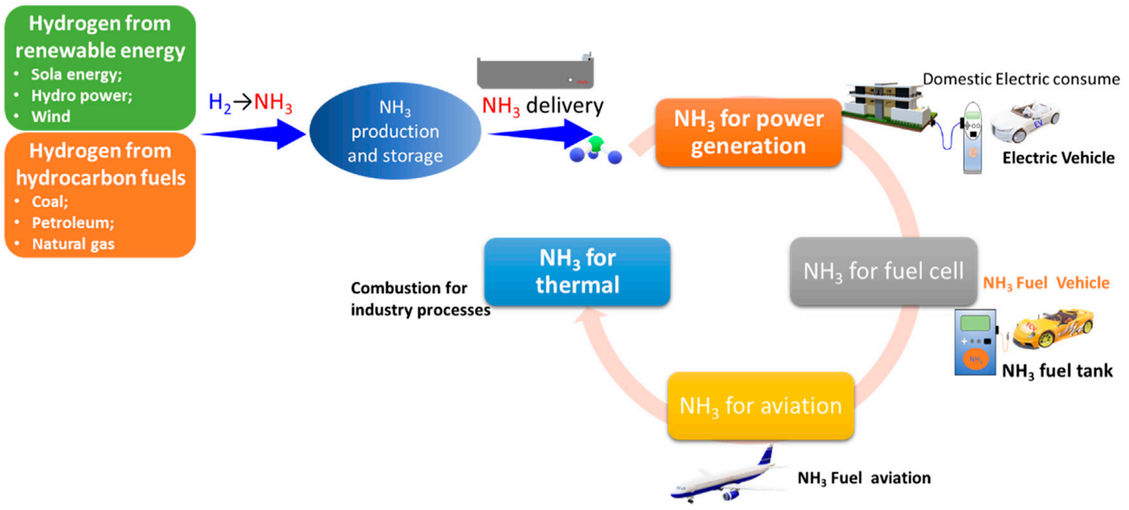

FIGURE 1 | Application of NH_3 as a near zero emission fuel system.

carbon-free fuel with the advantage of 1) CO_2, SO_x, and soot emission free; 2) production from various sources, such as fossil fuels, renewable sources, and biomass; 3) transport and storage with existing facility, such as fuel tanks, ships, trucks, and pipelines, which makes NH_3 as a favorable alternative fuel candidate (Wang et al., 2007; Zamfirescu and Dincer, 2008; Zamfirescu and Dincer, 2009; Andersson and Lundgren, 2014; Habgood et al., 2015; Afif et al., 2016; Chai et al., 2021). As shown in **Figure 1**, NH_3 is synthesized from energy sources such as wind power, nuclear energy, and fossil fuels with CO_2 capture and storage (CCS), etc., which means that NH_3 is fully CO_2 free recyclable as a promising carbon-free fuel.

The potential of NH_3 as a carbon-free fuel owing to its suitable storage and transportation properties has been demonstrated, and applications for its combustion in vehicular engines and turbines are apparent. However, major challenges for NH_3 combustion are to provide its alternative fuels capabilities with outstanding performance, durability and reliability, optimize combustion properties, and lower pollutant emissions, which needs a strict determination of combustion properties during the application of NH_3 as a fuel. The lack of understanding of the NH_3 combustion characteristics, methods of combustion enhancement, and optimization of NO_x formation in combustion have placed limits on the utilization of NH_3 as a fuel. It is necessary to have a comprehensive understanding of the combustion and emission characteristics of pure NH_3 and mixture with other fuels, which are expected to supply power for transport vehicles, electricity for power generation, and heating for industry with suitable combustion properties in future energy system.

PROPERTIES OF NH_3

As a carbon-free chemical compound, NH_3 is a colorless gas with a characteristic pungent smell. The chemical and physical properties of NH_3 are listed in **Table 1**. In 1909, German chemists Fritz Haber and Carl Bosch developed the NH_3 production process, now known as the Haber-Bosch process, which catalytically converts N_2 (from air) and H_2 (from industrial processes) to NH_3 using a metal catalyst under high-pressure (150–250 atm) and high-temperature (400–600°C) conditions. The production of NH_3 has dramatically increased in recent years. In 2020, the global NH_3 production was around 144 million metric ton (shown in **Figure 2**). The highest individual producers are China is (48.0 million ton: 33.3%), India (12.0 million ton: 8.3%), Russia (10.3 million ton: 7.2%), and the United States (9.2 million ton: 6.4%) (USGS, 2021). The majority of NH_3 is used in industrial and agricultural applications such as fertilizer, plastics, nitric acid, and explosives production, and refrigeration. NH_3 is a poisonous gas, and its safety hazard is a significant obstacle in its use. According to the US Department of Health and Human Services, the permissible exposure limit (PEL) for NH_3 is 35 ppm (27 mg m^{-3}) as a short-term (15 min) exposure limit (CDC, 1994).

TABLE 1 | Chemical and physical properties of gaseous NH_3 (NCBI, 2021).

Items	Symbols	Value	Unit
Molecular weight	M	17.031	g mol^{-1}
Critical temperature	T_{cr}	405.15	K
Critical pressure	P_{cr}	111.5	Atm
Density (STP)	P	0.769	kg m^{-3}
Viscosity (1 atm, 273 K)	M	9.8E-5	Poise
Heat capacity at constant P	C_p	0.037	kJ mol^{-1} K^{-1}
Heat capacity at constant V	C_v	0.028	kJ mol^{-1} K^{-1}
Thermal conductivity	Λ	0.002219	W m^{-1} K^{-1}
		18.65	MJ kg^{-1}
Lower heating value	LHV	3,080	MJ L^{-1}
		317.56	kJ mol
Autoignition temperature	T_{ig}	903	K
Lower flammability limit	LFL	15%	—
Upper flammability limit	UFL	27%	—

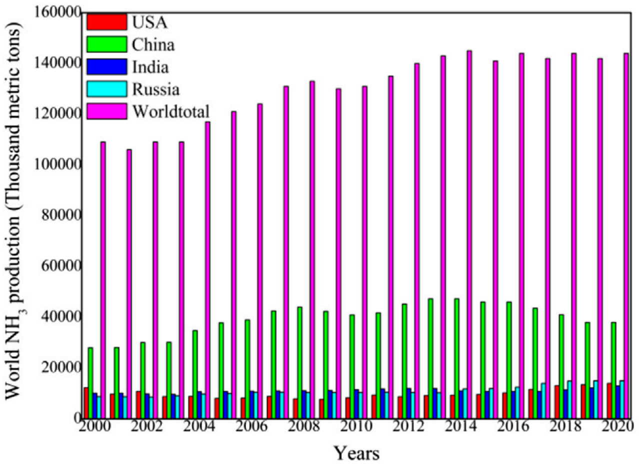

FIGURE 2 | World NH_3 production (Data from USGS, 2021).

Some characteristics of ammonia are compared with conventional liquefied fuels such as diesel, gasoline, and natural gas, which are listed in **Table 2** (Dimitriou and Javaid, 2020). The liquefied ammonia can be easily stored at 298 K and 10.2 atm. But the stored pressure of compressed liquid natural gas is 245.0 atm at 298 K, which is much higher than that of ammonia. Although the fuel density and energy density of ammonia are lower than those of gasoline and diesel, the fuel density of ammonia is three times as many as that of natural gas and the energy density is also much higher than that of natural gas. The octane rating of ammonia is 110 RON, which is higher than those of natural gas and gasoline. It indicates that the engine fueled by ammonia can be operated at higher pressure. What's more, ammonia exhibits much higher absolute minimum ignition energy than gasoline, which can be improved through some methods like co-firing with hydrogen. Ammonia has potential to be used as a fuel and the performance can be comparable to that of conventional fuel. For example, when directly using ammonia in an internal combustion engine, the driving range can reach 592 km, which is comparable to that of LPG and slightly lower than that of gasoline (Zamfirescu and Dincer, 2008).

NH_3 has been widely used in the industry. It has been used in the manufacture of fertilizers, in organic and inorganic synthesis of chemical compounds as HNO, urea, plastics fibers and so on, in mining and metallurgy, in petroleum refining as neutralizing agent, and also NH_3 can be used as commercial refrigerant in food processing, as a substitute for calcium in bisulfite pulping of wood, and to purify municipal and industrial water supplies. Effective methods such as process enclosure, local exhaust ventilation, general dilution ventilation, and personal protective equipment, should be followed in controlling worker exposures or lead of this substance when used it as a fuel.

The use of NH_3 as a fuel by adding it to methane (Williams et al., 1991; Bell et al., 2002; Sullivan et al., 2002; Henshaw et al., 2005; Barbas et al., 2015), diesel (Reiter and Kong, 2011; Gill et al., 2012), DME (Gross and Kong, 2013), and H_2 (Skreiberg et al., 2004; Mendiara and Glarborg, 2009; Mørch et al., 2011; Joo and Kwon, 2012; Um et al., 2013; Choi et al., 2015) has been investigated. NH_3 has often been used as an agent for decreasing NO_x emissions in industrial treatment processes through selective catalytic reactions (Xu et al., 2002; Grossale et al., 2009; Yun and Kim, 2013). For CH_4 combustion, both the CO and NO emissions decreased with increasing excess oxygen coefficient. A higher CO emission and lower NO emission would result from a decreased oxygen concentration in the oxidizer under the O_2/CO_2 combustion atmosphere. Conversely, a higher NO_x emission and a significantly lower CO emission are formed in oxy-fuel firing compared with those formed with air firing. CO and NO_x formation and decomposition would be completely different when NH_3 is added to carbon-based fuels. In the absence of NH_3 seeding combustion, the most important NO formation process for CH_4 combustion is prompt-NO formation, followed by the NNH, thermal-NO, and N_2O formation processes. When the combustion mixture is seeded with NH_3 at concentrations of several to several thousand ppm, fuel-NO formation becomes the dominant process; with higher NH_3 concentrations, a greater portion is converted to N_2 rather than to NO (Williams et al., 1991; Barbas et al., 2015). In the ignition engine, the addition of NH_3 leads to a longer ignition delay and limits the engine load because of the high autoignition temperature and low combustion rate (or low burning velocity). The combustion pressure and temperature would also be reduced with the addition of NH_3, leading to higher CO and HC emissions. NO_x formation would be enhanced because of NO_x formation from fuel-nitrogen when NH_3 is added. However, soot formation would be extremely low (Gross and Kong, 2013). Furthermore, the substitution of NH_3 could be favored, not only because of the replacement of the carbon-based fuel, but also because it is an efficient method for reducing overall CO_2 emissions (Gill et al., 2012; Gross and Kong, 2013).

TABLE 2 | Some characteristics of NH_3 versus natural gas, gasoline, and diesel (Dimitriou and Javaid, 2020).

Properties	Ammonia	Natural gas	Gasoline	Diesel	Units
Storage method	Compressed Liquid	Compressed Liquid	Liquid	Liquid	—
Storage temperature	298	298	298	298	K
Storage pressure	10.2	245.0	1.0	1.0	atm
Absolute minimum ignition energy	8	—	0.14	—	mJ
Fuel density	602.8	187.2	698.3	838.8	kg/m^3
Energy density	11,333	7,132	31,074	36,403	MJ/m^3
Octane rating	110	107	90–98	—	RON

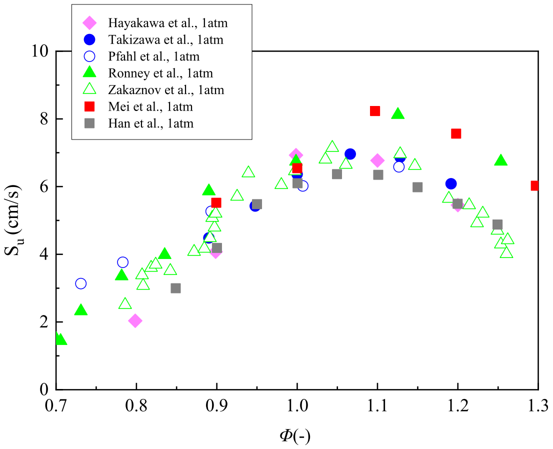

FIGURE 3 | Laminar burning velocity of NH_3 flame with a function of equivalence ratio at 298 K and 1 atm, replotted from (Han et al., 2019; Kobayashi et al., 2019; Mei et al., 2019).

LAMINAR BURNING VELOCITY OF NH_3

Laminar burning velocity is a significant important parameter during fuel combustion. The laminar burning velocity is the speed at which unburned gases move through the combustion wave in the direction normal to the wave surface, which can be calculated by the Metghalchi and Kech power-law relation as follows (Metghalchi and Keck, 1982):

$$S_u = S_{u0}\left(\frac{T_u}{T_0}\right)^{\alpha}\left(\frac{p}{p_0}\right)^{\beta} \tag{1}$$

where S_u is the laminar burning velocity (m/s), T_u is the unburned temperature (K), T_0 = 298 K, p is pressure (atm), p_0 = 1 atm, S_{u0}, α, and β are constants.

Many researches about laminar burning velocity of ammonia/air flames have been reported, most of which were studied under ambient condition (Zakaznov et al., 1978; Ronney, 1988; Pfahl et al., 2000; Takizawa et al., 2008; Hayakawa et al., 2015a; Han et al., 2019, Mei et al., 2019). Zakaznov et al. measured the burning velocity by cylindrical-tube method at room temperature and atmospheric pressure (Zakaznov et al., 1978). Ronney et al. measured the flame speed by a constant-volume cylindrical combustion vessel at microgravity condition (Ronney, 1988). Pfahl et al. measured the behavior of ammonia/air flames by using the schlieren system in a constant volume combustion vessel (Pfahl et al., 2000). In order to minimize the uncertainty caused by the buoyancy effect, they also measured the horizontal component of the flame motion. Takizawa et al. measured the laminar burning velocity using the spherical-vessel method in a constant volume combustion vessel (Takizawa et al., 2008). Hayakawa et al. measured the flame speed using high speed schlieren photography in a constant volume combustion chamber (Hayakawa et al., 2015a). Recently, Han et al. measured the flame propagation of ammonia/air by using heat flux method (Han et al., 2019). And the laminar burning velocities of ammonia/air mixtures was also investigated using a high-pressure constant-volume cylindrical combustion vessel by Mei et al. (2019). **Figure 3** shows the relationship between laminar burning velocities of NH_3/air flames and equivalence ratio at 298 K and 1 atm. The range of the flame velocity is roughly from 1.4 to 8.23 cm/s at φ = 0.7–1.3. It can be observed that the results measured by different groups reach their peaks around φ = 1.1, while the maximum values vary from 6.3 to 8.2 cm/s. The relative differences are little at lean conditions, however, a discrepancy more than 2 cm/s appears under fuel-rich condition between the experimental results. The burning velocity of NH_3/air flame is relatively low when compared with that of CH_4/air flame whose maximum value is about 35 cm/s (Law, 2006).

Ronney et al. measured the flame speed at p = 0.066, 0.132, 0.329, 1, and 1.974 atm. They found that the change of pressure had a modest influence on the flame velocity (Ronney, 1988). Duynslaegher et al. investigated the ammonia/air flame speed by using Konnov mechanism at T = 300K, P = 1–40 atm and φ = 1.0 (Duynslaegher et al., 2010). Results show an increase of pressure had a negative effect on the flame propagation, especially at the low pressure. With the pressure increased from 1 to 10 atm, the flame speed rapidly decreased from 12.67 cm/s to 8.15 cm/s. But with the pressure increased from 30 to 40 atm, the burning velocity decreased smoothly from 6.13 to 5.65 cm/s. Hayakawa et al. studied the laminar burning velocity of ammonia/air flames at elevated pressures by five detailed mechanism, which was validated by the measured experimental results (shown in **Figure 4**, Hayakawa et al., 2015a). **Figure 4** shows the laminar burning velocities under different initial pressure P_i and equivalence ratio φ, plotted along with simulation results by using Tian, Miller, Konnov, GRI 3.0, and Lindsted mechanism (Lindstedt et al., 1994; Miller et al., 1983; Frenklach et al., 2000; Konnov, 2009; Tian et al., 2009). The flame velocity decreases with the increase of initial pressure under the equivalence ratios of 0.9, 1.0, and 1.2. The tendency of the experimental and simulation results is the same as those of hydrocarbon. But it is different from the results of Ronney et al., which are indicated that pressure had a little influence on the flame speed (Ronney, 1988). The initial pressure has a larger effect on flame propagation speed at φ = 1. For example, as pressure increased from 1 to 5 atm, the laminar burning velocity of measured stoichiometric NH_3/air flame deceased from 6.9 to 4 cm/s (shown in **Figure 4B**), while the differences is about 1 cm/s at φ = 0.9 and 1.2 (shown in **Figures 4A,C**). As shown in **Figure 4**, most mechanism significantly over-predict the measured burning velocity. It is notable that the simulation results by Konnov mechanism is about two times larger than the measured values while the prediction results by GRI 3.0 mechanism closely agree with the experimental data. However, GRI 3.0 mechanism lacks some ammonia oxidation reactions which are very important for the numerical simulation of NO concentration in ammonia/air flame. Therefore, further improvements of those mechanisms are very necessary. Liu et al. experimentally and numerically studied the variations of laminar burning velocity with initial pressure for ammonia/air flame (Liu et al., 2019a). The flame speed has been measured at

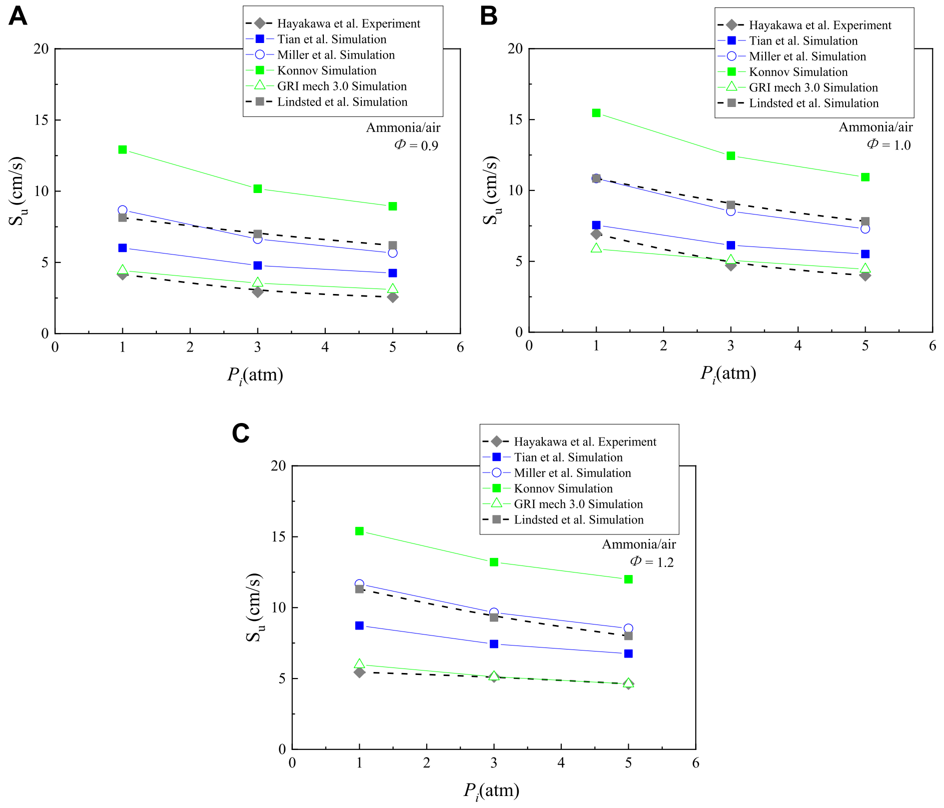

FIGURE 4 | Laminar burning velocity of NH_3 flame with a function of initial mixture pressure at φ = 0.9, 1 and 1.2, replotted from (Hayakawa et al., 2015a).

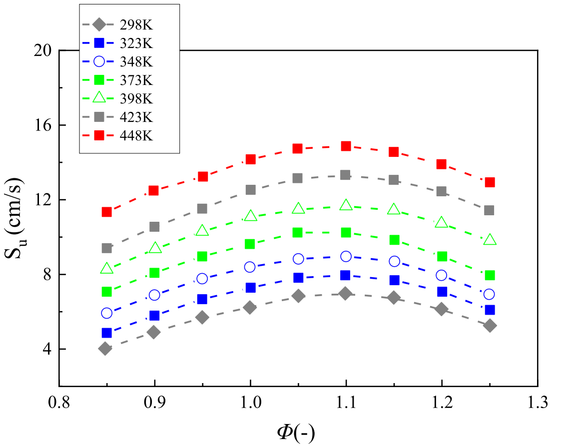

FIGURE 5 | Laminar burning velocity of NH_3 flame with a function of equivalence ratio at various temperature, replotted from (Han et al., 2020).

initial pressure from 0.3 to 1.6 atm, covering equivalence ratios from 0.5 to 1.3 and at 298 K. The measured laminar burning velocities of NH_3 flame firstly increased slightly and then decreased with the increasing pressure. The burning velocity of stoichiometric flame reaches the peak value at 0.5 atm. The maximum values exist at 0.7 atm when the equivalence ratio is 0.5 or 1.3. Generally, the laminar burning velocity decreases with an increase in pressure, which is agreeable with the observation obtained by Hayakawa et al. (2015a). The numerical simulation was calculated by using the GRI 3.0 mechanism under initial pressure ranged from 0.3 to 1.6 atm, and equivalence ratio of 1.0 and temperature of 298 K. The difference between the measurements and the calculations is around 12 cm/s.

The influence of temperature is rarely investigated. Cohen measured the laminar burning velocity of ammonia/air flame at temperature ranged from 323 to 423 K by using a flat flame burner (Cohen, 1955). Recently, Lhuillier et al. measured the flame speed at 1 atm and temperature from 298 to 473 K by the spherical flame method (Lhuillier et al., 2020a). Han et al. measured the laminar burning velocity of NH_3 flame using the heat flux method at temperature from 298 to 448 K and 1 atm (shown in **Figure 5**, Han et al., 2020). Li et al. numerically investigated the effect of preheating temperature on the combustion and NO emission characteristics of ammonia flame (Li et al., 2016a; Li et al., 2016b). In all temperature ranges, the laminar burning velocities increase firstly before the equivalence ratio reaches 1.1, and then decrease when the equivalence ratio is large than 1.1. The maximum value of flame speed at different temperatures ranges from 6.98 to 14.87 cm/s. With the temperature increasing, the flame speed exponentially increases. The results measured by Han et al. at 423 K were compared with those from Cohen and Lhuillier (Cohen, 1955;

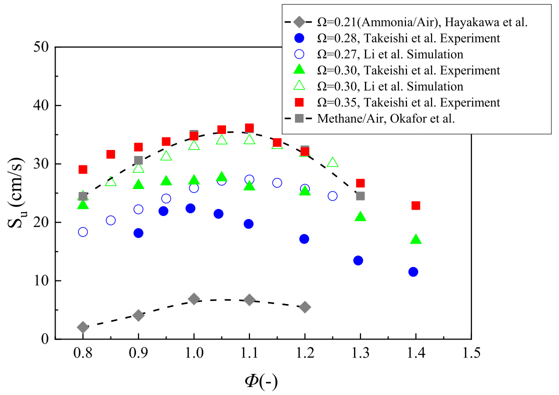

FIGURE 6 | Laminar burning velocity of NH_3 flame with a function of equivalence ratio at various oxygen enrichment level, replotted from (Hayakawa et al., 2015a, Takeishi et al., 2015; Li et al., 2015; Okafor et al., 2018; Kobayashi et al., 2019).

Han et al., 2020; Lhuillier et al., 2020b). It was found that the experimental values obtained by Han et al. are lower than those from Cohen and Lhuillier. The difference between the measurements is around 2 cm/s, which is larger at fuel-lean conditions. The simulation results by using five mechanisms were also performed. Comparison of numerical and experimental data showed that the simulations results by using Okafor mechanism (Okafor et al., 2018) and Otomo mechanism (Otomo et al., 2018) performed best.

Oxygen enriched combustion can be considered as a promising approach to increase burning velocity. The experimental results measured by Takeishi are shown in **Figure 6** (Takeishi et al., 2015). It can be observed that the velocities can be close to those of CH_4/air flames when the O_2 concentration up to 0.35 and the maximum velocity improves to 36.1 cm/s, which is around 5 times the value measured under the air condition. Li et al. (2015) numerically investigated the effect of the oxygen content towards the burning velocity of NH_3/air flame by using the Millar mechanism (Millar and Bowman, 1989) and the Reductive Konnov mechanisms (Duynslaegher et al., 2009; Duynslaegher et al., 2012). The maximum laminar burning velocity increases from 27.5 to 33.9 cm/s when the O_2 content increases from 0.27 to 0.30, and the values of laminar burning velocity at the O_2 content of 0.30 are always 6–7 cm/s higher than those at the O_2 content of 0.27. It is mainly due to an increase of the reaction rates of OH, H, O, and NH_2 radicals under a higher O_2 concentration. It is found that the laminar burning velocities calculated by Li et al. are over-predicted when compared with the results of Takeishi's experiment at the O_2 content of 0.30, especially at fuel rich conditions. For example, the difference between experimental and numerical results reaches 7.9 cm/s at the equivalence ratio of 1.1, while the discrepancy is around 1.5 cm/s at the equivalence ratio of 0.8. Recently, it was found that the burning velocities of ammonia are proper for the practical applications when the range of O_2 volume concentration in O_2/N_2 mixture is roughly from 0.35 to 0.40 (Kim et al., 2021). Mei et al. measured the ammonia/air flame speed under the O_2 content ranged from 0.21 to 0.45 at 298 K, the pressure ranged from 1 to 5 atm and the equivalence ratios from 0.7 to 1.5 by using more complicated constant pressure spherical flame method (Mei et al., 2019). The flame speed increases with an increase of the O_2 concentration, but decrease with an increase of initial pressure. The experimental results showed that the flame propagation speeds are lower than those of CH_4/air flames at the O_2 concentration of 0.35. It is different from the results of Takeishi et al., which indicated that the laminar burning velocities at the O_2 concentration of 0.35 are almost the same as those of CH_4/air flames (Takeishi et al., 2015). In addition, they constructed a model of ammonia combustion with 38 species and 265 reactions, which can predict the results with a favorable satisfaction. Wang et al. measured the oxy-ammonia flame speed in a constant volume vessel at the temperatures ranged from 303 to 393 K, the O_2 content ranged from 0.6 to 1.0 and the equivalence ratios ranged from 0.6 to 1.4 (Wang et al., 2020). Results show that the peak value of laminar burning velocity can reach 125.1 cm/s at the O_2 content of 1.0. The equivalence ratio corresponding maximum value is around 0.9. Besides, the flame velocity increases with the increasing temperature, which is more sensitive to the change of temperature under lower O_2 content.

Due to low burning velocity, ammonia usually is burned with the addition possessing higher reactivity such as hydrogen. Ichikawa et al. measured the ammonia/hydrogen/air flame speed at pressure of 1, 3, and 5 atm by using a high-pressure constant volume chamber (shown in **Figure 7**, Ichikawa et al., 2015). The experimental results show an exponential variation of laminar burning velocity under different volumetric hydrogen fraction and the ammonia/hydrogen/air flame speed decreased with an increase in pressure under the same hydrogen concentration. It is obvious that the laminar burning velocity largely decreased when the pressure increased from 1 to 3 atm, while the values of burning velocities at 3 atm were almost the same as those of flame speeds at 5 atm. This means that the influence of initial pressure conspicuously appeared under low pressure, but that effects barely occurred under high pressure. Lee

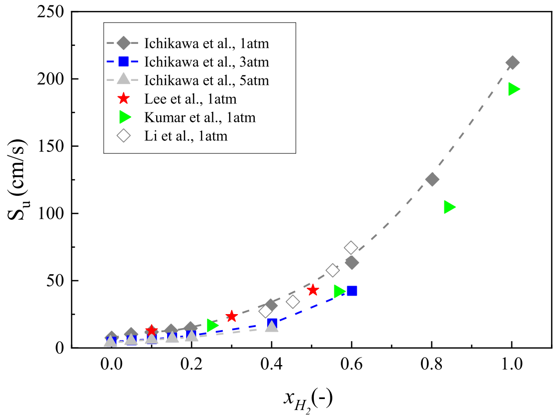

FIGURE 7 | Laminar burning velocity of NH_3 flame with a function of volumetric hydrogen fraction at 298 K, replotted from (Lee et al., 2010; Kumar and Meyer, 2013; Li et al., 2014; Ichikawa et al., 2015).

et al., Kumar et al., and Li et al. also investigated the flame propagation speed of ammonia/hydrogen/air mixture at 1 atm (Lee et al., 2010; Kumar and Meyer, 2013; Li et al., 2014; Li et al., 2017; Li et al., 2019a). The differences among experimental results were small and the tendencies were consistent with that measured by Ichikawa et al. (2015). It also can be observed that the value of flame speed was around 35.1 cm/s at the hydrogen concentration of 0.45 which was close to that of CH_4/air mixture, indicating that the addition of hydrogen can effectively improve ammonia combustion. Han et al. measured the laminar burning velocities of NH_3/H_2/air by using the heat flux method (covering φ = 0.7–1.6, χ_{H_2} = 0.15–0.4, P = 1atm, K = 298 K) (Han et al., 2019). Results show that the values of measurements reached their peaks at φ = 1.05 when the hydrogen ratio ranged from 0 to 0.35. However, the peak velocity occurred at the equivalence ratio of 1.1 when the hydrogen ratio increased up to 0.4. This tendency has good agreement with the finding that the peak value of the hydrogen/air flame speed occurs at the equivalence ratio of 1.8 (Kwon and Faeth, 2001). They also found that mixing ammonia with the addition of H_2 is the most effective way to improve the flame propagation by comparing with the burning velocity of NH_3/CH_4 mixture, NH_3/H_2 mixture, and NH_3/CO mixture. The flame speeds of NH_3/H_2 flames (the hydrogen concentration ranged from 0.0 to 0.3) and pure ammonia at oxygen rich conditions (the oxygen concentration ranged from 0.21 to 0.30) were measured by Shrestha et al. at P = 1–10 atm and T = 298–473 K (Shrestha et al., 2021). They also developed a mechanism for the oxidation of ammonia/hydrogen mixtures and ammonia. Based on this model, they found that the N_2H_2 formation path was favored in fuel rich condition, which is very important for numerical simulation.

Different from adding hydrogen, hydrogen production can also be from ammonia decomposition, since ammonia has high hydrogen density (Valera-Medina et al., 2018; Kobayashi et al., 2019). It was found that ammonia started to crack when the temperature reached 473.15 K and the conversion efficiency can reach 98–99% when the temperature up to 698.15 K (Klerke et al., 2008; Lan et al., 2012). What's more, in contrast to co-firing hydrogen, using partially cracked ammonia is more economical and easier to implement (Yang et al., 2019). However, the deep insight into the combustion characteristics of $NH_3/H_2/N_2$ mixtures are limited (Mei et al., 2021; Wiseman et al., 2021). Very recently, Mei et al. experimentally investigated the laminar burning velocities of partially cracked NH_3/air mixtures in a high-pressure constant volume cylindrical combustion vessel at the initial pressure of 1–10 atm, the equivalence ratios from 0.7 to 1.4 and the initial temperature of 298 K (Mei et al., 2021). Results showed that the laminar flame speed of $NH_3/H_2/N_2$/air mixtures increased with an increase of the cracking ratio due to the increase of H_2 concentration. It was found that the flame speed could reach 38.1 cm/s at 1 atm and the cracking ratio of 40%, which is close to that of methane/air mixtures. They also found that the increase of N_2 concentration and the initial pressure had a negative effect on the flame speed. Then though the numerical simulation, they recognized that $H + O_2 (+M) = HO_2 (+M)$ plays an important in flame propagation.

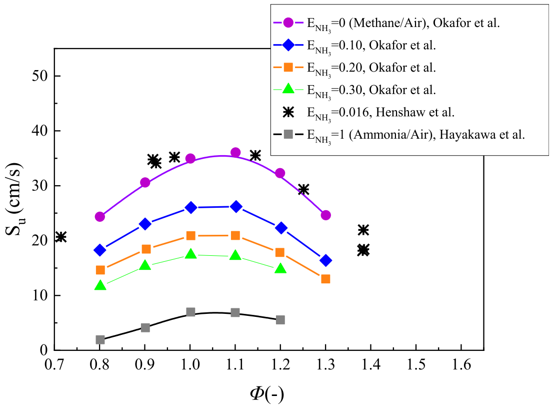

FIGURE 8 | Laminar burning velocity of NH_3 flame with a function of equivalence ratio at various ammonia addition in Methane/ammonia/air flames, replotted from (Okafor et al., 2018; Henshaw et al., 2005; Hayakawa et al., 2015a).

Blending ammonia with methane is also an effective method to improve the combustion characteristics of NH_3/air flames propagation. Konnov et al. experimentally investigated the laminar burning velocity of $CH_4/O_2/N_2$ flames doped with 0.5% NH_3 by using a heat flux method. Results show that ammonia had no significant influence on the flame speed (Konnov et al., 2006). Okafor et al. and Henshaw et al. measured the flame speeds of NH_3/CH_4/air flames as a function of the equivalence ratio at 298 K and 1 atm (Henshaw et al., 2005; Okafor et al., 2018). Zhou et al. experimentally and numerically investigated the laminar flames of NH_3/syngas/air and NH_3/bio-syngas/air at elevated temperature (Zhou et al., 2021). Wang et al. experimentally and numerically investigated the laminar burning velocities of NH_3 mixing with CH_3OH and C_2H_5OH in premixed flames (Wang et al., 2021a). **Figure 8** shows that the flame speeds decreased with the heat fraction of ammonia E_{NH3} increased and the flame speed were close to those of methane/air mixture when E_{NH3} reached 0.016. Obviously, the burning velocity decreased more sharply when E_{NH3} ranged from 0 to 0.1. The difference between the flame speed at $E_{NH3} = 0.1$ and $E_{NH3} = 0.3$ is about 8.8 cm/s, while the discrepancy is around 9.8 cm/s when the E_{NH3} increases from 0 to 0.1. Xiao et al. investigated the laminar burning velocity of NH_3/CH_4 mixtures with the ammonia fraction ranged from 0 to 100% (Xiao et al., 2017b). They also found that ammonia had a negative impact on flame propagation. Shu et al. studied the fundamental combustion characteristics of NH_3/CH_4/air mixtures by using expending spherical flames (Shu et al., 2021). They found that the laminar burning velocity varied almost linearly with the methane volume fraction and the H/OH radicals were very important for the propagation of flames under fuel lean conditions. Furthermore, the laminar burning velocity had a strong linear relationship with the maximum mole fraction of (H + OH) radicals under lean conditions when the pressure ranged from 1 to 15 atm and the methane volume fraction ranged from 0.30 to 0.70. The laminar burning velocity of ammonia/methane mixture under variable O_2 and CO_2 mole fractions of

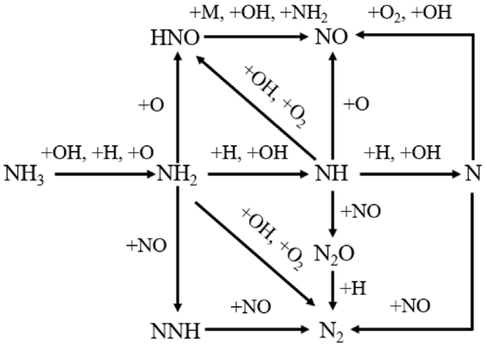

FIGURE 9 | Diagram of ammonia oxidation pathway, replotted from (Millar and Bowman, 1989).

0.35–0.40 and 0.45 to 0.65, respectively, was experimentally investigated by Liu et al. (2019b). They found that the maximum flame speed decreased from 35.6 to 25.6 cm/s when the CO_2 mole fraction increased from 0.45 to 0.65, while the peak speed increased from 25.6 to 36.6 cm/s when the O_2 concentration increased from 0.35 to 0.40. Through the simulation results by using HUST Mechanism, it can be observed that the burning velocity has linear correlations between CO_2 and O_2 concentration.

NO_X EMISSIONS

When ammonia is completely combusted, it only produces nitrogen and water without involving the production of NO_x. However, NO_x emission is relatively high in practical combustion, which is a main challenge of ammonia combustion. In order to reduce the production of NO_x, some detailed mechanism of ammonia combustion is necessary. NO_x is mainly composed of thermal NO_x and fuel NO_x. Thermal NO is usually produced by the oxidation of N_2 at temperature up to 1800 K. The extended Zeldovich mechanism is widely used to describe the formation of thermal NO. The reactions of thermal NO have three important pathways: $N_2 + O = NO + N$, $N + O_2 = NO + O$, and $N + OH = NO + H$. The first reaction limits the reaction rate and usually take place when the temperature above 1,800 K. Therefore, controlling temperature is an effective way to reduce thermal NO production.

Fuel NO_x emission is widely studied by many researchers. Miller et al. studied the reaction path of NH_3 oxidation and proposed a kinetics including 22 species and 98 elementary reactions (shown as **Figure 9**, Millar and Bowman, 1989). Firstly, ammonia is converted to NH_2 by the reaction with OH, which is the primary path under both fuel rich and lean conditions. It is also consumed by O to produce NH_2 under fuel lean condition and is consumed by H under rich condition. The reason of this phenomenon is that rich burning flame needs more oxygen or oxygen atoms, which results in the proportion of H in O/H radicals is high when compared to fuel lean conditions (Chai et al., 2021). It is obvious that the reactions involving NH_i (i = 0, 1, 2) have very significant impact on the formation and reduction of NO. And HNO intermediate make great contribution to NO formation via reacting with OH, NH_2, and M. Lindstedt et al. also found that fuel NO is mainly produced by the reactions involving HNO (Lindstedt et al., 1994). For ammonia flames, $HNO + M = NO + H + M$ reaction plays a key role and $HNO + OH = NO + H_2O$ reaction becomes important when the equivalence ratio less than 1. What's more, for the conversion of NO, the reaction between NO and NH_2 is the major path.

Dean et al. found that NNH dissociation plays an important role in the formation of N_2 under fuel rich conditions, which mainly produced by N_2H_2 (Dean et al., 1984). The NH_i radicals can be converted to N_2 without including NO, which has a potential to reduce the formation of NO. They developed the NNH mechanism (Dean and Bozzelli, 2000). The reaction between NNH intermediate and O atom is the main path to generate NO, and the related reaction are shown as follow: $NNH + O = NH + NO$, $NNH + O = N_2O + H$, and $NNH + O = N_2 + OH$. Klippenstein et al. calculated the reaction rate constant of NNH by using an improved model based on the Miller mechanism (Miller and Glarborg, 1999; Klippenstein et al., 2011). They found that the rate constant of $NNH + O = N_2 + OH$ is over-predicted by Dean et al. and the NNH + O reaction is very fast.

Some factors like equivalence ratio and pressure are also very important for NO_x emissions. The main component of NO_x is NO. It was found that with an increase of the equivalence ratio, the mole fraction of NO in NH_3/air flame firstly increased before the equivalence ratio reaches 0.9 and then rapidly decreased when the equivalence ratio is large than 0.9 (Kobayashi et al., 2019). The production of NO is extremely low after the equivalence ratio up to 1.3. Therefore, it seems that burning under fuel rich condition is an effective way to reduce NO_x emission. Hayakawa et al. experimentally and numerically studied the characteristics of

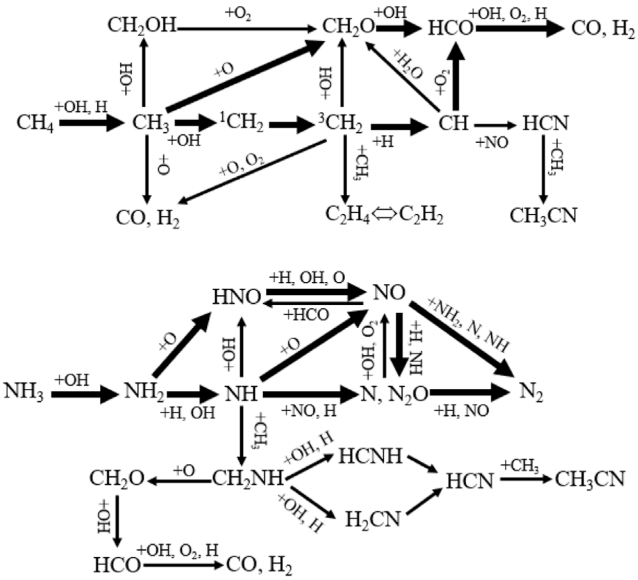

FIGURE 10 | Diagram of ammonia/methane mixture oxidation pathway, replotted from (Tian et al., 2009).

NO_x formation in ammonia/air flames at different pressures and equivalence ratios (covering p = 1.0–3.0 atm and φ = 0.7–1.1) (Hayakawa et al., 2015b). The experiments were performed in a nozzle-type burner and the numerical simulation used the Tian mechanism (Tian et al., 2009). Results show that the NO concentration decreased with an increasing equivalence ratio at pressure of 1 atm, which is mainly due to surplus production of NH_i (i = 0, 1, 2) under fuel rich conditions. Besides, with the increasing pressure, the concentration of NO decreased while the reaction rate of $OH + H + M = H_2O + M$ increased. Therefore, they proposed that H and OH radicals mentioned above limited the formation of NO.

In order to use pure ammonia in practical applicants, some researches were performed to provide a deep insight into the characteristic of NO_x emission. Lee et al. proposed a combustion strategy in order to use pure ammonia in the internal combustion engine (Lee and Song, 2018). In this strategy, they injected the lean ammonia/air mixture during the intake process which was auto-ignited in the next step. This method can raise the temperature and pressure of the cylinder and it has a positive effect on ammonia spray combustion. Then they studied the mechanism of NO formation and found that NO emission in this engine largely depend on the main SOI variation. For instance, the maximum value of NO formation up to 8,500 ppm, while the reduction of NO emission can reach 5,460 ppm by changing the SOI timing. Kurata studied the emission characteristics of non-premixed NH_3/air in gas turbine power generations (Kurata et al., 2017). It was found that the production of NO_x and slip NH_3 were strongly influenced by the combustor inlet temperature. The existence of NO_x and slip NH_3 at the mid-range of combustor inlet temperature implied that there is a possibility of NO reduction through selective non-catalytic reduction. They also developed a low-NO_x NH_3-air non-premixed combustor for actual gas-turbine operations and found that the NO production of this gas turbine power generation could be lowered to 337 ppm when O_2 content reached 16% (Kurata et al., 2019). Okafor et al. designed a two-stage combustor for a micro gas turbine and found that NO_x emission was around 42 ppm at initial pressure of 3 atm and initial temperature of 298K when the equivalence ratio of the primary stage reached 1.1 and the equivalence ratio of the secondary stage was 0.4 (Okafor et al., 2019). Somarathne et al. numerically investigated the NO_x and NH_3 emission of turbulent premixed ammonia/air flames in a gas turbine like combustor by using the large eddy simulation at elevated pressure up to 5 atm and various equivalence ratios (Somarathne et al., 2017). They found that NO production decreased when the initial pressure increased and the minimum value of NO and unburnt NH_3 emission could reach 200 ppm at initial pressure of 5 atm and the equivalence ratio of 1.2. What's more, the NO emission of ammonia/air flames with the secondary air injection could be lowered to 100 ppm at O_2 content of 16%. Rocha et al. numerically studied the NO_x emission characteristics of ammonia/air mixtures under the typical conditions of commercial gas turbines by using three modern stationary gas turbine concepts (Rocha et al., 2020). They found that rich-burn, quick-quench and lean-burn (RQL) concept and moderate or intense low oxygen dilution (MILD) concept are able to reach low NO_x emission while the NO_x emission by using lean-burn dry-low emissions (DLE) concept is high.

There are also some researches about the NO_x emission of NH_3/H_2/air flames. Li et al. experimentally measured the NO_x concentration of NH_3/H_2/air flames covering the NH_3 concentration from 0.440 to 0.544 at the equivalence ratios from 1.00 to 1.25 (Li et al., 2014). They found that NO_x emission decreased when the equivalence ratio increased from 1.00 to 1.25 under different NH_3 contents. It can be observed that a more significant change occurs when the equivalence ratio increased from 1.00 to 1.10, while the change is small when the equivalence ratio increased from 1.10 to 1.25. As the NH_3 concentration increase the production of NO_x decrease, which due to the low flame temperature. The peak value of NO_x content is 1,450 ppm at NH_3 content of 0.500 and stoichiometric condition, while the maximum content is around 1,660 ppm when NH_3 content of NH_3/H_2 mixture reaches 0.416 under stoichiometric condition. They also concluded that fuel NO_x plays a significant role in NO_x emission, whereas thermal NO_x is negligible. Nozari et al. also studied the variation of the NO_x emission with the equivalence ratio at elevated pressure of 17 atm and temperature of 673 K (Nozari, 2015). They found that the NO_x concentration increased first and then decreased when the equivalence ratio ranged from 0.5 to 1.2 in all hydrogen content ranges. The maximum mole fraction of NO_x occurred under fuel lean conditions, which is similar to that of ammonia/air flames. Wang et al. also found that the NO concentration in exhaust gas was non-monotonically changed with equivalence ratios and hydrogen mole ratio, because the competition between the effects by the reduction of N-atom and the enrichment of H/O radicals when hydrogen is added to ammonia flame (Wang et al., 2021b). Lee et al. also found that both NO_x and N_2O emissions are low in fuel rich condition when compared to those under lean conditions (Lee et al., 2010).

The influences of pressure and hydrogen content on NO_x emissions are also significant. Xiao et al. numerically investigated the influence of pressure in NH_3/H_2 flames by using an improved mechanism based on the work performed by Mathieu et al. (Mathieu and Petersen, 2015; Xiao et al., 2017a). Results show that the concentration of NO_x significantly decreased with an increasing pressure. NO_x emission can be less than 5 ppm when the pressure reaches 10 atm and less than 1 ppm when the pressure up to 20 atm. Rocha et al. numerically investigated the variation of NO_x emission with hydrogen addition ratio ranged from 0 to 1 by ten mechanisms for ammonia/hydrogen/air flames at 1 atm and 298 K (Rocha et al., 2019). Results show that with an increase of the H_2 content, the NO_x emission increased before the mole fraction of H_2 reached 0.80 and then rapidly decreased when the mole fraction of H_2 large than 0.80. They presumed that the presence of OH/O radicals at high temperature resulted in the increasing content of NO_x before the H_2 concentration reached 0.80, while the decreasing concentration of ammonia leads to the decrease of NO_x when the mole fraction of H_2 large than 0.80.

Lhuillier et al. experimentally investigated the NO_x emission of NH_3/H_2/air mixtures in spark ignition engine at the intake temperature of 323 K and pressure of 1.2 atm (Lhuillier et al., 2020a). It was found that NO_x production firstly increased and then decreased with an increased of the equivalence ratio. The peak values of NO_x formation occurred at the equivalence ratio of 0.8–0.9 and the minimal NO_x emission was found under rich conditions. What's more, as the H_2 concentration of NH_3/H_2/air mixtures increased, the emission increased. Very recently, Franco et al. also designed a laboratory combustor which had good performance in NO_x emission (Franco et al., 2021). Valera-Medina et al. numerically and experimentally investigated the NO_x emission of premixed 50%NH_3/50%H_2 mixtures under fuel lean condition in a swirl combustor and found that the pollution emission was high when compared with that under fuel rich condition (Valera-Medina et al., 2017). Then they studied characteristics of 70%NH_3/30%H_2 mixtures under gas turbine conditions through a numerical GT cycle model and found that NO_x emission could as low as 50 ppm because the hot unburned ammonia was able to react with NO_x (Valera-Medina et al., 2019). Hussein et al. found that injecting some NH_3/H_2 blend downstream the primary zone could significantly reduce the NO_x emission which was a promising method to minimize the pollution emission (Hussein et al., 2019).

Recently, many researches have studied the NO_x emission of CH_4/NH_3 flames. Among them, Tian mechanism is widely used to predict the NO_x emission of CH_4/NH_3 mixtures, which has a satisfactory prediction of the experimental results (Tian et al., 2009). Tian et al. investigated the intermediates and products for ammonia/methane/air/Ar flames at 0.04 atm and $\varphi = 1$ by using tunable synchrotron vacuum ultraviolet photoionization and molecular-beam mass spectrometry (Tian et al., 2009). Results show that the formation of NO_2 decreased while those of NO and N_2 increased with the mole ratios of NH_3/CH_4 increasing from 0 to 1. They also developed a detailed mechanism including 84 species and 703 elementary reactions, which can predict the major combustion species and intermediates well (shown as **Figure 10**). The process of CO formation is described below. Firstly, methane is converted to CH_3 by the reaction with OH and H. Then CH_3 mainly reacts with O addition to generate CH_2O and reacts with OH to form singlet CH_2 which can transform to triplet CH_2. CH_2 is converted to CH by reacting with H and then CH transforms to HCO by reacting with O_2. Besides, HCO also can be produced by the reaction of CH_2O with OH. Finally, HCO is converted to CO and H_2 by reacting with OH, O_2, and H. However, NO is produced by the reaction of NH with O and the reaction of HNO with H, OH, and O. It seems that the addition of CH_4 has no significant influence on the major formation and reduction of NO. Though the numerical simulation, it also can be found that four reactions including $H + O_2 = O + OH$, $NH_2 + O = HNO + H$, $NH_2 + NO = N_2 + H_2O$, and $NH + NO = N_2O + H$ are important for the conversion of NO and N_2.

Ramos et al. measured the NO_x emissions from CH_4/NH_3 flames at NH_3 content ranged from 0 to 0.7 and the equivalence ratio of 0.8, 0.9, and 1 by using a laboratory scale laminar flame burner (Filipe Ramos et al., 2019). They found that the production of NO_x firstly increased and then slightly decreased with an increasing NH_3 content and the maximum NO_x emission occurred when the concentration of NH_3 reached 0.50. Xiao et al. numerically studied the emission characteristics of CH_4/NH_3 mixtures at the ammonia ratio from 0 to 1 by using an improved model based on the Konnov mechanism and found the same tendency (Konnov, 2009; Xiao et al., 2017b). It was found that the addition of ammonia had a significant positive effect on NO_x emission under high methane proportion mixtures while it had a negative effect under high ammonia concentration. The probable reason of this phenomenon is that $H + NO = HNO$ inhibits the formation of NO at high ammonia concentration (Rocha et al., 2021). The equivalence ratio and initial pressure also has a strong impact on NO_x emission. Ramos et al. found that the peak values of the NO_x concentration are around 4,300, 3,600, and 2,800 ppm at the equivalence ratio of 1, 0.9, and 0.8, respectively, (Filipe Ramos et al., 2019). It is obvious that NO_x emissions decrease with a decrease of the equivalence ratio. Xiao et al. also studied the influence of the equivalence ratio and found that the maximum NO_x emission is presented at the equivalence ratio of 0.9 when the ammonia mole fraction ranged from 0.20 to 0.80 (Xiao et al., 2017b). Then they numerically studied the reaction involving NO by using Tian mechanism (Xiao et al., 2020). It was found that $NH_2+O=HNO + H$ reaction is the most promoting reaction at $\varphi = 0.8$, while $H + O_2 = O + OH$ is the most promoting reaction at $\varphi = 1, 1.2$. The most inhibiting reaction is $NH_2+NO = N_2+H_2O$, $NH + NO = N_2O + H$, $NH_2+NO = NNH + OH$ at $\varphi = 0.8$, 1 and 1.2, respectively. For NO_x emission, the initial pressure plays an important role. The NO mole fraction decreased with the increasing pressure and the NO production was more sensitive to the change of the pressure than CO (Xiao et al., 2017b). What's more, it was found that the formation of NO is mainly through the $NH + OH = HNO + H$ reaction at high pressure (Valera-Medina et al., 2017). Zhang et al. investigated the emission characteristics of ammonia/air combustion in a model combustor with the addition of methane and hydrogen. They found NO and OH radicals showed a positive correlation, and the temperature had a secondary role on promoting NO_x formation comparing with CH_4/air flame (Zhang et al., 2021a). The thermal performance and NO_x emission on a premixed methane/ammonia/flame at a micro-planar combustor were also investigated. Results showed that ammonia addition reduced CO_2 emission, but increased NO emission increased. While N_2O emission increased first and then decreased with increasing ammonia ratio. (Cai et al., 2020; Cai et al., 2021; Han et al., 2021; Sun et al., 2021). An et al. found that the OH and NO were closely correlated in premixed CH_4/NH_3/air flames as they were both strongly related to flame temperature. While N_2O had a correlation with NH and HNO components (An et al., 2021), which is similar with the results by the same combustion group. (Zhang et al., 2020; Zhang et al., 2021b; Wei et al., 2021).

Recently, CH_4/NH_3 blends are also considered as a substitute fuel in practical applications. Liquefied natural gas is an alternative fuel and has been widely used in marine engines (Schinas and Butler, 2016). What's more, it also can improve the poor combustion characteristics of pure ammonia. Therefore, Oh et al. investigated the pollution emission of ammonia mixed with methane and found that NO_x emissions of CH_4/NH_3 blends in spark ignited engine rapidly increased before the split ratio of NH_3 reached 40% and then slightly decreased when the split ratio large than 40% (Oh et al., 2021). Besides, the maximum NO_x emission of this study was lower than 40 g/kWh. Xiao et al. compared the simulation results under gas turbine conditions by using Tian, Konnov, Mendiara, GRI 3.0 and ÅA mechanism and found that Tian mechanism performed best in NO_x prediction (Xiao et al., 2017c, Tian et al., 2009, Mendiara and Glarborg, 2009, GRI, 2000, Åbo Akademi University, 2005). What's more, they found that the oxidation of N and HNO played the most important role in the production of NO under gas turbine conditions. Li et al. also studied the NO_x emission of CH_4/NH_3 mixtures under gas turbine conditions and recognized that NO_x formation increased when the NH_3 concentration increased, which is mainly due to the enhanced HNO pathway (Li et al., 2019b). Furthermore, they found that the availability of oxygen has significant influence on the production of NO_x through HNO pathway and proposed a combustion system in which NO_x production can as low as 30 ppm even when the NH_3 concentration up to 40%. Okafor et al. used rich-lean combustion to control NO_x emission and proposed the optimum equivalence ratio of the primary zone ranged from 1.30 to 1.35 (Okafor et al., 2020). This method can significantly reduce the formation of NO_x, for instance, NO_x emission can be lowered to 49ppm. Okafor et al. investigated the characteristics of liquid NH_3 spray co-fired with CH_4 and found that the minimum NO_x emission occurred when the equivalence ratio reached 1.06 (Okafor et al., 2021a). They also studied the NO_x emission characteristics of this kind of fuel in two-stage micro gas turbine combustors and recognized that the increased inlet temperature and decreased wall heat loss led to the reduction of NO and N_2O (Okafor et al., 2021b).

CONCLUSIONS AND PERSPECTIVES

This paper presents the burning velocity and pollutant emissions of NH_3 flames, NH_3/H_2 flames and CH_4/NH_3 flames. At 1 atm and 298 K, the laminar burning velocities increase before the equivalence ratio reaches 1.1, and then decrease when the equivalence ratio is large than 1.1. The maximum value of laminar burning velocity is less than 10 cm/s, which is relatively low when compared with that of CH_4/air flame. Under different pressure conditions, it can be found that the flame velocity decreases with an increase of the initial pressure. The influence of temperature is also studied. With the initial temperature increasing, the flame speed exponentially increases. In order to increase the laminar burning velocity of NH_3/air flames, oxygen enriched combustion is proposed as a promising approach. The flame speed of NH_3/air flames under oxygen enrichment conditions increases with an increase of the O_2 concentration, but decrease with an increase of initial pressure under oxygen enrichment conditions. And the flame velocity increases with the increasing temperature, which is more sensitive to the change of temperature under lower O_2 content. Besides, ammonia is usually burned with the additions of hydrogen and methane to improve the combustion characteristics. The addition of H_2 or CH_4 can significantly increase the flame speed.

NO_x is composed of the thermal NO_x and the fuel NO_x, which is the major pollution of ammonia combustion. Thermal NO_x is usually produced by the oxidation of N_2 when the temperature reaches 1,800 K. The generation of the thermal NO is satisfactorily described by the extended Zeldovich mechanism. It can be reduced by controlling temperature. Fuel NO_x is mainly generated by the oxidation of NH_3. HNO intermediate plays an important role in NO formation by reacting with OH and NH_2. It was found that burning under rich condition and high pressure can effectively reduce NO_x emission. The effects of equivalence ratio and pressure in NH_3/H_2 flames are similar to those of NH_3/air flames. The NO_x production firstly increased with an increase of the H_2 content before the H_2 concentration reached 0.8, and then rapidly decreased after the mole fraction of H_2 large than 0.8. The reaction pathways in the combustion of NH_3/CH_4 fuels are described by using Tian mechanism. It seems that the addition of CH_4 has no significant influence on the major formation and reduction of NO. The NO_x production is high under high ammonia content, high temperature and stoichiometric condition. What's more, the concentration of CO_2 also influences the formation of NO_x. The high CO_2 content has a positive impact on NO_x production under fuel rich condition, while has a negative effect under stoichiometric and lean conditions.

Although the fundamental characteristics of ammonia-based flames has been widely studied, the practical application of this kind of fuel is still unsatisfying. Therefore, further studies are needed to overcome the problems, including low burning velocities and high NO_x emission. For example, one of the main challenges in the investigation of ammonia-based fuel is that the numerical simulations by using mechanisms usually overpredict or underpredict when compared with those are obtained during the actual combustion processing. In order to fully understand the combustion characteristics of ammonia-based flames, developing an accurate mechanism is necessary. What's more, for emission characteristics of CH_4/NH_3 mixtures, many researches focused on reducing NO_x emission, and few studies on the carbon capture can be found. Therefore, it still need further studied.

AUTHOR CONTRIBUTIONS

Conceptualization, JL, HH, and NK; literature review and resources, JL, SL, DC, RW, and LD; writing, JL and SL; review and editing, HH and NK; funding acquisition, JL and HH. All authors have read and agree to the published version of the article.

FUNDING

This work was supported by Leading Key Projects of Chinese Academy of Sciences (No.QYZDY-SSW-JSC038), Key Special Project for Introduced Talents Team of Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou) (GML2019ZD0108), and Science and Technology Planning Project of Guangdong Province, China (No. 2017A050501046).

REFERENCE

Åbo Akademi University (2005). Åbo Akademi (ÅA) Scheme. Available at: http://www.abo.fi/fakultet/ookforskkinetschem (Accessed Oct 5, 2020).

Afif, A., Radenahmad, N., Cheok, Q., Shams, S., Kim, J. H., and Azad, A. K. (2016). Ammonia-fed Fuel Cells: a Comprehensive Review. *Renew. Sustain. Energ. Rev.* 60, 822–835. doi:10.1016/j.rser.2016.01.120

An, Z., Zhang, M., Zhang, W., Mao, R., Wei, X., Wang, J., et al. (2021). Emission Prediction and Analysis on CH_4/NH_3/air Swirl Flames with LES-FGM Method. *Fuel* 304, 121370. doi:10.1016/j.fuel.2021.121370

Andersson, J., and Lundgren, J. (2014). Techno-economic Analysis of Ammonia Production via Integrated Biomass Gasification. *Appl. Energ.* 130, 484–490. doi:10.1016/j.apenergy.2014.02.029

Astbury, G. R. (2008). A Review of the Properties and Hazards of Some Alternative Fuels. *Process Saf. Environ. Prot.* 86, 397–414. doi:10.1016/j.psep.2008.05.001

Barbas, M., Costa, M., Vranckx, S., and Fernandes, R. X. (2015). Experimental and Chemical Kinetic Study of CO and NO Formation in Oxy-Methane Premixed Laminar Flames Doped with NH_3. *Combust. Flame* 162, 1294–1303. doi:10.1016/j.combustflame.2014.10.020

Bell, J. B., Day, M. S., Grcar, J. F., Bessler, W. G., Schulz, C., Glarborg, P., et al. (2002). Detailed Modeling and Laser-Induced Fluorescence Imaging of Nitric Oxide in a NH_3-seeded Non-premixed Methane/air Flame. *Proc. Combust. Inst.* 29, 2195–2202. doi:10.1016/s1540-7489(02)80267-x

Cai, T., Zhao, D., Wang, B., Li, J., and Guan, Y. (2020). NO Emission and thermal Performances Studies on Premixed Ammonia-Oxygen Combustion in a CO_2-free Micro-planar Combustor. *Fuel* 280, 118554. doi:10.1016/j.fuel.2020.118554

Cai, T., Zhao, D., Li, X., Shi, B., and Li, J. (2021). Mitigating NO Emissions from an Ammonia-Fueled Micro-power System with a Perforated Plate Implemented. *J. Hazard. Mater.* 401, 123848. doi:10.1016/j.jhazmat.2020.123848

CDC (1994). Immediately Dangerous to Life or Health Concentrations. Centers for Disease Control and Prevention. Available at: https://www.cdc.gov/niosh/idlh/7664417.html (Accessed Dec 24, 2020).

Chai, W. S., Bao, Y., Jin, P., Tang, G., and Zhou, L. (2021). A Review on Ammonia, Ammonia-Hydrogen and Ammonia-Methane Fuels. *Renew. Sustain. Energ. Rev.* 147, 111254. doi:10.1016/j.rser.2021.111254

Choi, S., Lee, S., and Kwon, O. C. (2015). Extinction Limits and Structure of Counterflow Nonpremixed Hydrogen-Doped Ammonia/air Flames at Elevated Temperatures. *Energy* 85, 503–510. doi:10.1016/j.energy.2015.03.061

Cohen, L. (1955). Burning Velocities of Ammonia in Air and in Oxygen. *Fuel* 34, S123–S127. doi:10.1002/j.2164-4918.1955.tb01284.x

da Rocha, R. C., Costa, M., and Bai, X.-S. (2019). Chemical Kinetic Modelling of Ammonia/hydrogen/air Ignition, Premixed Flame Propagation and NO Emission. *Fuel* 246, 24–33. doi:10.1016/j.fuel.2019.02.102

Dean, A. M., and Bozzelli, J. W. (2000). "Combustion Chemistry of Nitrogen," in *Gas-Phase Combustion Chemistry* (New York: Springer), 125–341. doi:10.1007/978-1-4612-1310-9_2

Dean, A. M., Chou, M.-S., and Stern, D. (1984). Kinetics of Rich Ammonia Flames. *Int. J. Chem. Kinet.* 16, 633–653. doi:10.1002/kin.550160603

Dimitriou, P., and Javaid, R. (2020). A Review of Ammonia as a Compression Ignition Engine Fuel. *Int. J. Hydrogen Energ.* 45, 7098–7118. doi:10.1016/j.ijhydene.2019.12.209

Duynslaegher, C., Jeanmart, H., and Vandooren, J. (2009). Flame Structure Studies of Premixed Ammonia/hydrogen/oxygen/argon Flames: Experimental and Numerical Investigation. *Proc. Combust. Inst.* 32, 1277–1284. doi:10.1016/j.proci.2008.06.036

Duynslaegher, C., Jeanmart, H., and Vandooren, J. (2010). Ammonia Combustion at Elevated Pressure and Temperature Conditions. *Fuel* 89, 3540–3545. doi:10.1016/j.fuel.2010.06.008

Duynslaegher, C., Contino, F., Vandooren, J., and Jeanmart, H. (2012). Modeling of Ammonia Combustion at Low Pressure. *Combust. Flame* 159, 2799–2805. doi:10.1016/j.combustflame.2012.06.003

Filipe Ramos, C., Rocha, R. C., Oliveira, P. M. R., Costa, M., and Bai, X.-S. (2019). Experimental and Kinetic Modelling Investigation on NO, CO and NH_3 Emissions from NH_3/CH_4/air Premixed Flames. *Fuel* 254, 115693. doi:10.1016/j.fuel.2019.115693

Franco, M. C., Rocha, R. C., Costa, M., and Yehia, M. (2021). Characteristics of NH_3/H_2/air Flames in a Combustor Fired by a Swirl and bluff-body Stabilized Burner. *Proc. Combust. Inst.* 38, 5129–5138. doi:10.1016/j.proci.2020.06.141

Frenklach, M., Bowman, T., and Smith, G. (2000). GRI-Mech 3.0. Available at: http://www.me.berkeley.edu/gri-mech/index.html (Accessed Jan 7, 2021).

Gill, S. S., Chatha, G. S., Tsolakis, A., Golunski, S. E., and York, A. P. E. (2012). Assessing the Effects of Partially Decarbonising a Diesel Engine by Co-fuelling with Dissociated Ammonia. *Int. J. Hydrogen Energ.* 37, 6074–6083. doi:10.1016/j.ijhydene.2011.12.137

Gross, C. W., and Kong, S.-C. (2013). Performance Characteristics of a Compression-Ignition Engine Using Direct-Injection Ammonia-DME Mixtures. *Fuel* 103, 1069–1079. doi:10.1016/j.fuel.2012.08.026

Grossale, A., Nova, I., and Tronconi, E. (2009). Ammonia Blocking of the "Fast SCR" Reactivity over a Commercial Fe-Zeolite Catalyst for Diesel Exhaust Aftertreatment. *J. Catal.* 265, 141–147. doi:10.1016/j.jcat.2009.04.014

Habgood, D. C. C., Hoadley, A. F. A., and Zhang, L. (2015). Techno-economic Analysis of Gasification Routes for Ammonia Production from Victorian Brown Coal. *Chem. Eng. Res. Des.* 102, 57–68. doi:10.1016/j.cherd.2015.06.008

Han, X., Wang, Z., Costa, M., Sun, Z., He, Y., and Cen, K. (2019). 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* 206, 214–226. doi:10.1016/j.combustflame.2019.05.003

Han, X., Wang, Z., He, Y., Liu, Y., Zhu, Y., and Konnov, A. A. (2020). The Temperature Dependence of the Laminar Burning Velocity and Superadiabatic Flame Temperature Phenomenon for NH_3/air Flames. *Combust. Flame* 217, 314–320. doi:10.1016/j.combustflame.2020.04.013

Han, L., Li, J., Zhao, D., Xi, Y., Gu, X., and Wang, N. (2021). Effect Analysis on Energy Conversion Enhancement and NO_x Emission Reduction of Ammonia/hydrogen Fuelled Wavy Micro-combustor for Micro-thermophotovoltaic Application. *Fuel* 289, 119755. doi:10.1016/j.fuel.2020.119755

Hayakawa, A., Goto, T., Mimoto, R., Arakawa, Y., Kudo, T., and Kobayashi, H. (2015a). Laminar Burning Velocity and Markstein Length of Ammonia/air Premixed Flames at Various Pressures. *Fuel* 159, 98–106. doi:10.1016/j.fuel.2015.06.070

Hayakawa, A., Goto, T., Mimoto, R., Kudo, T., and Kobayashi, H. (2015b). NO Formation/reduction Mechanisms of Ammonia/air Premixed Flames at Various Equivalence Ratios and Pressures. *Mech. Eng. J.* 2, 14–00402. doi:10.1299/mej.14-00402

Henshaw, P. F., D'Andrea, T., Mann, K. R. C., and Ting, D. S.-K. (2005). Premixed Ammonia-Methane-Air Combustion. *Combust. Sci. Techn.* 177, 2151–2170. doi:10.1080/00102200500240695

Hussein, N. A., Valera-Medina, A., and Alsaegh, A. S. (2019). Ammonia-Hydrogen Combustion in a Swirl Burner with Reduction of NO_x Emissions. *Energ. Proced.* 158, 2305–2310. doi:10.1016/j.egypro.2019.01.265

Ichikawa, A., Hayakawa, A., Kitagawa, Y., Kunkuma Amila Somarathne, K. D., Kudo, T., and Kobayashi, H. (2015). Laminar Burning Velocity and Markstein Length of Ammonia/hydrogen/air Premixed Flames at Elevated Pressures. *Int. J. Hydrogen Energ.* 40, 9570–9578. doi:10.1016/j.ijhydene.2015.04.024

IEA (2021). *Global Energy Review 2021*. Paris: International Energy Agency. Available at: https://www.iea.org/reports/global-energy-review-2021.

Joo, J. M., Lee, S., and Kwon, O. C. (2012). Effects of Ammonia Substitution on Combustion Stability Limits and NO_x Emissions of Premixed Hydrogen-Air Flames. *Int. J. Hydrogen Energ.* 37, 6933–6941. doi:10.1016/j.ijhydene.2012.01.059

Kim, H. K., Ku, J. W., Ahn, Y. J., Kim, Y. H., and Kwon, O. C. (2021). Effects of O_2 Enrichment on NH_3/air Flame Propagation and Emissions. *Int. J. Hydrogen Energ.* 46 (46), 23916–23926. doi:10.1016/j.ijhydene.2021.04.154

Klerke, A., Christensen, C. H., Nørskov, J. K., and Vegge, T. (2008). Ammonia for Hydrogen Storage: Challenges and Opportunities. *J. Mater. Chem.* 18, 2304–2310. doi:10.1039/b720020j

Klippenstein, S. J., Harding, L. B., Glarborg, P., and Miller, J. A. (2011). The Role of NNH in NO Formation and Control. *Combust. Flame* 158, 774–789. doi:10.1016/j.combustflame.2010.12.013

Kobayashi, H., Hayakawa, A., Somarathne, K. D. K. A., and Okafor, E. C. (2019). Science and Technology of Ammonia Combustion. *Proc. Combust. Inst.* 37, 109–133. doi:10.1016/j.proci.2018.09.029

Konnov, A. A., Dyakov, I. V., and De Ruyck, J. (2006). Probe Sampling Measurements of No in $Ch_4+O_2+N_2$ Flames Doped with NH_3. *Combust. Sci. Techn.* 178 (6), 1143–1164. doi:10.1080/00102200500296788

Konnov, A. A. (2009). Implementation of the NCN Pathway of Prompt-NO Formation in the Detailed Reaction Mechanism. *Combust. Flame* 156, 2093–2105. doi:10.1016/j.combustflame.2009.03.016

Kumar, P., and Meyer, T. R. (2013). Experimental and Modeling Study of Chemical-Kinetics Mechanisms for H_2-NH_3-air Mixtures in Laminar Premixed Jet Flames. *Fuel* 108, 166–176. doi:10.1016/j.fuel.2012.06.103

Kurata, O., Iki, N., Matsunuma, T., Inoue, T., Tsujimura, T., Furutani, H., et al. (2017). Performances and Emission Characteristics of NH_3-air and NH_3CH_4-air Combustion Gas-Turbine Power Generations. *Proc. Combust. Inst.* 36, 3351–3359. doi:10.1016/j.proci.2016.07.088

Kurata, O., Iki, N., Inoue, T., Matsunuma, T., Tsujimura, T., Furutani, H., et al. (2019). Development of a Wide Range-Operable, Rich-Lean Low-NO_x Combustor for NH_3 Fuel Gas-Turbine Power Generation. *Proc. Combust. Inst.* 37, 4587–4595. doi:10.1016/j.proci.2018.09.012

Kwon, O. C., and Faeth, G. M. (2001). Flame/stretch Interactions of Premixed Hydrogen-Fueled Flames: Measurements and Predictions. *Combust. Flame* 124, 590–610. doi:10.1016/s0010-2180(00)00229-7

Lan, R., Irvine, J. T. S., and Tao, S. (2012). Ammonia and Related Chemicals as Potential Indirect Hydrogen Storage Materials. *Int. J. Hydrogen Energ.* 37, 1482–1494. doi:10.1016/j.ijhydene.2011.10.004

Law, C. K. (2006). *Combustion Physics*. Cambridge: Cambridge University Press, 347.

Lee, D., and Song, H. H. (2018). Development of Combustion Strategy for the Internal Combustion Engine Fueled by Ammonia and its Operating Characteristics. *J. Mech. Sci. Technol.* 32 (4), 1905–1925. doi:10.1007/s12206-018-0347-x

Lee, J. H., Kim, J. H., Park, J. H., and Kwon, O. C. (2010). Studies on Properties of Laminar Premixed Hydrogen-Added Ammonia/air Flames for Hydrogen Production. *Int. J. Hydrogen Energ.* 35 (3), 1054–1064. doi:10.1016/j.ijhydene.2009.11.071

Lhuillier, C., Brequigny, P., Contino, F., and Mounaïm-Rousselle, C. (2020a). Experimental Study on Ammonia/hydrogen/air Combustion in Spark Ignition Engine Conditions. *Fuel* 269, 117448. doi:10.1016/j.fuel.2020.117448

Lhuillier, C., Brequigny, P., Lamoureux, N., Contino, F., and Mounaïm-Rousselle, C. (2020b). Experimental Investigation on Laminar Burning Velocities of Ammonia/hydrogen/air Mixtures at Elevated Temperatures. *Fuel* 263, 116653. doi:10.1016/j.fuel.2019.116653

Li, J., Huang, H., Kobayashi, N., He, Z., and Nagai, Y. (2014). Study on Using Hydrogen and Ammonia as Fuels: Combustion Characteristics and NO_x formation. *Int. J. Energ. Res.* 38, 1214–1223. doi:10.1002/er.3141

Li, J., Huang, H., Kobayashi, N., He, Z., Osaka, Y., and Zeng, T. (2015). Numerical Study on Effect of Oxygen Content in Combustion Air on Ammonia Combustion. *Energy* 93, 2053–2068. doi:10.1016/j.energy.2015.10.060

Li, J., Huang, H., Yuan, H., Zeng, T., Yagami, M., and Kobayashi, N. (2016a). Modelling of Ammonia Combustion Characteristics at Preheating Combustion: NO Formation Analysis. *IJGW* 10, 230–241. doi:10.1504/ijgw.2016.077915

Li, J., Huang, H., Kobayashi, N., He, Z., Osaka, Y., and Zeng, T. (2016b). Research on Combustion and Emission Characteristics of Ammonia under Preheating Conditions. *J. Chem. Eng. Jpn.* 49, 641–648. doi:10.1252/jcej.15we075

Li, J., Huang, H., Kobayashi, N., Wang, C., and Yuan, H. (2017). Numerical Study on Laminar Burning Velocity and Ignition Delay Time of Ammonia Flame with Hydrogen Addition. *Energy* 126, 796–809. doi:10.1016/j.energy.2017.03.085

Li, J., Huang, H., Deng, L., He, Z., Osaka, Y., and Kobayashi, N. (2019a). Effect of Hydrogen Addition on Combustion and Heat Release Characteristics of Ammonia Flame. *Energy* 175, 604–617. doi:10.1016/j.energy.2019.03.075

Li, S., Zhang, S., Zhou, H., and Ren, Z. (2019b). Analysis of Air-Staged Combustion of NH_3/CH_4 Mixture with Low NO_x Emission at Gas Turbine Conditions in Model Combustors. *Fuel* 237, 50–59. doi:10.1016/j.fuel.2018.09.131

Lindstedt, R. P., Lockwood, F. C., and Selim, M. A. (1994). Detailed Kinetic Modelling of Chemistry and Temperature Effects on Ammonia Oxidation. *Combust. Sci. Techn.* 99, 253–276. doi:10.1080/00102209408935436

Liu, Q., Chen, X., Huang, J., Shen, Y., Zhang, Y., and Liu, Z. (2019a). The Characteristics of Flame Propagation in Ammonia/oxygen Mixtures. *J. Hazard. Mater.* 363, 187–196. doi:10.1016/j.jhazmat.2018.09.073

Liu, S., Zou, C., Song, Y., Cheng, S., and Lin, Q. (2019b). Experimental and Numerical Study of Laminar Flame Speeds of CH_4/NH_3 Mixtures under Oxy-Fuel Combustion. *Energy* 175, 250–258. doi:10.1016/j.energy.2019.03.040

Mathieu, O., and Petersen, E. L. (2015). Experimental and Modeling Study on the High-Temperature Oxidation of Ammonia and Related NO_x Chemistry. *Combust. Flame* 162 (3), 554–570. doi:10.1016/j.combustflame.2014.08.022

Mei, B., Zhang, X., Ma, S., Cui, M., Guo, H., Cao, Z., et al. (2019). Experimental and Kinetic Modeling Investigation on the Laminar Flame Propagation of Ammonia under Oxygen Enrichment and Elevated Pressure Conditions. *Combust. Flame* 210, 236–246. doi:10.1016/j.combustflame.2019.08.033

Mei, B., Zhang, J., Shi, X., Xi, Z., and Li, Y. (2021). Enhancement of Ammonia Combustion with Partial Fuel Cracking Strategy: Laminar Flame Propagation and Kinetic Modeling Investigation of $NH_3/H_2/N_2$/air Mixtures up to 10 Atm. *Combust. Flame* 231, 111472. doi:10.1016/j.combustflame.2021.111472

Mendiara, T., and Glarborg, P. (2009). Ammonia Chemistry in Oxy-Fuel Combustion of Methane. *Combust. Flame* 156, 1937–1949. doi:10.1016/j.combustflame.2009.07.006

Metghalchi, M., and Keck, J. C. (1982). Burning Velocities of Mixtures of Air with Methanol, Isooctane, and Indolene at High Pressure and Temperature. *Combust. Flame* 48, 191–210. doi:10.1016/0010-2180(82)90127-4

Miller, J. A., and Bowman, C. T. (1989). Mechanism and Modeling of Nitrogen Chemistry in Combustion. *Prog. Energ. Combust. Sci.* 15, 287–338. doi:10.1016/0360-1285(89)90017-8

Miller, J. A., and Glarborg, P. (1999). Modeling the thermal De-NO_x Process: Closing in on a Final Solution. *Int. J. Chem. Kinet.* 31, 757–765. doi:10.1002/(sici)1097-4601(1999)31:11<757:aid-jck1>3.0.co;2-v

Miller, J. A., Smooke, M. D., Green, R. M., and Kee, R. J. (1983). Kinetic Modeling of the Oxidation of Ammonia in Flames. *Combust. Sci. Techn.* 34, 149–176. doi:10.1080/00102208308923691

Mørch, C. S., Bjerre, A., Gøttrup, M. P., Sorenson, S. C., and Schramm, J. (2011). Ammonia/hydrogen Mixtures in an SI-Engine: Engine Performance and Analysis of a Proposed Fuel System. *Fuel* 90, 854–864.

NCBI (2021). PubChem-Ammonia. National Center for Biotechnology Information. Available at: https://pubchem.ncbi.nlm.nih.gov/compound/222 (Accessed May 15, 2021).

Nozari, H., and Karabeyoğlu, A. (2015). Numerical Study of Combustion Characteristics of Ammonia as a Renewable Fuel and Establishment of Reduced Reaction Mechanisms. *Fuel* 159, 223–233. doi:10.1016/j.fuel.2015.06.075

Oh, S., Park, C., KimKim, S. Y., Kim, Y., Choi, Y., and Kim, C. (2021). Natural Gas-Ammonia Dual-Fuel Combustion in Spark-Ignited Engine with Various Air-Fuel Ratios and Split Ratios of Ammonia under Part Load Condition. *Fuel* 290, 120095. doi:10.1016/j.fuel.2020.120095

Okafor, E. C., Naito, Y., Colson, S., Ichikawa, A., Kudo, T., Hayakawa, A., et al. (2018). Experimental and Numerical Study of the Laminar Burning Velocity of CH_4-NH_3-air Premixed Flames. *Combust. Flame* 187, 185–198. doi:10.1016/j.combustflame.2017.09.002

Okafor, E. C., Somarathne, K. D. K. A., Hayakawa, A., Kudo, T., Kurata, O., Iki, N., et al. (2019). Towards the Development of an Efficient Low-NO_x Ammonia Combustor for a Micro Gas Turbine. *Proc. Combust. Inst.* 37, 4597–4606. doi:10.1016/j.proci.2018.07.083

Okafor, E. C., Somarathne, K. D. K. A., Ratthanan, R., Hayakawa, A., Kudo, T., Kurata, O., et al. (2020). Control of NO_x and Other Emissions in Micro Gas Turbine Combustors Fuelled with Mixtures of Methane and Ammonia. *Combust. Flame* 211, 406–416. doi:10.1016/j.combustflame.2019.10.012

Okafor, E. C., Kurata, O., Yamashita, H., Inoue, T., Tsujimura, T., Iki, N., et al. (2021a). Liquid Ammonia spray Combustion in Two-Stage Micro Gas Turbine Combustors at 0.25 MPa; Relevance of Combustion Enhancement to Flame Stability and NO_x Control. *Appl. Energ. Combust. Sci.* 7, 100038. doi:10.1016/j.jaecs.2021.100038

Okafor, E. C., Yamashita, H., Hayakawa, A., Somarathne, K. D. K. A., Kudo, T., Tsujimura, T., et al. (2021b). Flame Stability and Emissions Characteristics of Liquid Ammonia spray Co-fired with Methane in a Single Stage Swirl Combustor. *Fuel* 287, 119433. doi:10.1016/j.fuel.2020.119433

Otomo, J., Koshi, M., Mitsumori, T., Iwasaki, H., and Yamada, K. (2018). Chemical Kinetic Modeling of Ammonia Oxidation with Improved Reaction Mechanism for Ammonia/air and Ammonia/hydrogen/air Combustion. *Int. J. Hydrogen Energ.* 43, 3004–3014. doi:10.1016/j.ijhydene.2017.12.066

Pfahl, U. J., Ross, M. C., Shepherd, J. E., Pasamehmetoglu, K. O., and Unal, C. (2000). Flammability Limits, Ignition Energy, and Flame Speeds in H_2-CH_4-NH_3-N_2O-O_2-N_2 mixtures. *Combust. Flame* 123, 140–158.

Reiter, A. J., and Kong, S.-C. (2011). Combustion and Emissions Characteristics of Compression-Ignition Engine Using Dual Ammonia-Diesel Fuel. *Fuel* 90, 87–97. doi:10.1016/j.fuel.2010.07.055

Rocha, R. C., Costa, M., and Bai, X. S. (2020). Combustion and Emission Characteristics of Ammonia under Conditions Relevant to Modern Gas Turbines. *Combust. Sci. Technol.*, 1–20. doi:10.1080/00102202.2020.1748018

Rocha, R. C., Zhong, S., Xu, L., Bai, X.-S., Costa, M., Cai, X., et al. (2021). Structure and Laminar Flame Speed of an Ammonia/methane/air Premixed Flame under Varying Pressure and Equivalence Ratio. *Energy Fuels* 35 (9), 7179–7192. doi:10.1021/acs.energyfuels.0c03520

Ronney, P. D. (1988). Effect of Chemistry and Transport Properties on Near-Limit Flames at Microgravity. *Combust. Sci. Techn.* 59, 123–141. doi:10.1080/00102208808947092

Schinas, O., and Butler, M. (2016). Feasibility and Commercial Considerations of LNG-Fueled Ships. *Ocean Eng.* 122, 84–96. doi:10.1016/j.oceaneng.2016.04.031

Shrestha, K. P., Lhuillier, C., Barbosa, A. A., Brequigny, P., Contino, F., Mounaïm-Rousselle, C., et al. (2021). 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.* 38, 2163–2174. doi:10.1016/j.proci.2020.06.197

Shu, T., Xue, Y., Zhou, Z., and Ren, Z. (2021). An Experimental Study of Laminar Ammonia/methane/air Premixed Flames Using Expanding Spherical Flames. *Fuel* 290, 120003. doi:10.1016/j.fuel.2020.120003

Skreiberg, Ø., Kilpinen, P., and Glarborg, P. (2004). Ammonia Chemistry below 1400 K under Fuel-Rich Conditions in a Flow Reactor. *Combust. Flame* 136, 501–518. doi:10.1016/j.combustflame.2003.12.008

Somarathne, K. D. K. A., Hatakeyama, S., Hayakawa, A., and Kobayashi, H. (2017). 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 Energ.* 42, 27388–27399. doi:10.1016/j.ijhydene.2017.09.089

Sullivan, N., Jensen, A., Glarborg, P., Day, M. S., Grcar, J. F., Bell, J. B., et al. (2002). Ammonia Conversion and NO_x Formation in Laminar Coflowing Nonpremixed Methane-Air Flames. *Combust. Flame* 131, 285–298. doi:10.1016/s0010-2180(02)00413-3

Sun, Y., Cai, T., and Zhao, D. (2021). Thermal Performance and NO_x Emission Characteristics Studies on a Premixed Methane-Ammonia-Fueled Micro-planar Combustor. *Fuel* 291, 120190. doi:10.1016/j.fuel.2021.120190

Takeishi, H., Hayashi, J., Kono, S., Arita, W., Iino, K., and Akamatsu, F. (2015). Characteristics of ammonia/N_2/O_2 Laminar Flame in Oxygen-Enriched Air Condition. *Trans. JSME* 81, 14–00423. doi:10.1299/transjsme.14-00423

Takizawa, K., Takahashi, A., Tokuhashi, K., Kondo, S., and Sekiya, A. (2008). Burning Velocity Measurements of Nitrogen-Containing Compounds. *J. Hazard. Mater.* 155, 144–152. doi:10.1016/j.jhazmat.2007.11.089

Tian, Z., Li, Y., Zhang, L., Glarborg, P., and Qi, F. (2009). An Experimental and Kinetic Modeling Study of Premixed NH_3/CH_4/O_2/Ar Flames at Low Pressure. *Combust. Flame* 156, 1413–1426. doi:10.1016/j.combustflame.2009.03.005

Um, D. H., Joo, J. M., Lee, S., and Kwon, O. C. (2013). Combustion Stability Limits and NO_x Emissions of Nonpremixed Ammonia-Substituted Hydrogen-Air Flames. *Int. J. Hydrogen Energ.* 38, 14854–14865. doi:10.1016/j.ijhydene.2013.08.140

USGS (2021). Nitrogen Statistics and Information. U. S. Geological Survey. Available at: https://www.usgs.gov/centers/nmic/nitrogen-statistics-and-information (Accessed May 20, 2021).

Valera-Medina, A., Pugh, D. G., Marsh, P., Bulat, G., and Bowen, P. (2017). Preliminary Study on Lean Premixed Combustion of Ammonia-Hydrogen for Swirling Gas Turbine Combustors. *Int. J. Hydrogen Energ.* 42, 24495–24503. doi:10.1016/j.ijhydene.2017.08.028

Valera-Medina, A., Xiao, H., Owen-Jones, M., David, W. I. F., and Bowen, P. J. (2018). Ammonia for Power. *Prog. Energ. Combust. Sci.* 69, 63–102. doi:10.1016/j.pecs.2018.07.001

Valera-Medina, A., Gutesa, M., Xiao, H., Pugh, D., Giles, A., Goktepe, B., et al. (2019). Premixed Ammonia/hydrogen Swirl Combustion under Rich Fuel Conditions for Gas Turbines Operation. *Int. J. Hydrogen Energ.* 44, 8615–8626. doi:10.1016/j.ijhydene.2019.02.041

Wang, F., Zhou, Z., Dai, Z., Gong, X., Yu, G., Liu, H., et al. (2007). Development and Demonstration Plant Operation of an Opposed Multi-Burner Coal-Water Slurry Gasification Technology. *Front. Energ. Power Eng. China* 1, 251–258. doi:10.1007/s11708-007-0035-5

Wang, D., Ji, C., Wang, Z., Wang, S., Zhang, T., and Yang, J. (2020). Measurement of Oxy-Ammonia Laminar Burning Velocity at normal and Elevated Temperatures. *Fuel* 279, 118425. doi:10.1016/j.fuel.2020.118425

Wang, D., Ji, C., Wang, S., Yang, J., and Wang, Z. (2021a). Numerical Study of the Premixed Ammonia-Hydrogen Combustion under Engine-Relevant Conditions. *Int. J. Hydrogen Energ.* 46, 2667–2683. doi:10.1016/j.ijhydene.2020.10.045

Wang, Z., Han, X., He, Y., Zhu, R., Zhu, Y., Zhou, Z., et al. (2021b). Experimental and Kinetic Study on the Laminar Burning Velocities of NH_3 Mixing with CH_3OH and C_2H_5OH in Premixed Flames. *Combust. Flame* 229, 111392. doi:10.1016/j.combustflame.2021.02.038

Wei, X., Zhang, M., An, Z., Wang, J., Huang, Z., and Tan, H. (2021). Large Eddy Simulation on Flame Topologies and the Blow-Off Characteristics of Ammonia/air Flame in a Model Gas Turbine Combustor. *Fuel* 298, 120846. doi:10.1016/j.fuel.2021.120846

Williams, W. R., Zhao, J., and Schmidt, L. D. (1991). Ignition and Extinction of Surface and Homogeneous Oxidation of NH_3 and CH_4. *AIChE J.* 37, 641–649. doi:10.1002/aic.690370502

Wiseman, S., Rieth, M., Gruber, A., Dawson, J. R., and Chen, J. H. (2021). A Comparison of the Blow-Out Behavior of Turbulent Premixed Ammonia/hydrogen/nitrogen-Air and Methane-Air Flames. *Proc. Combust. Inst.* 38, 2869–2876. doi:10.1016/j.proci.2020.07.011

Xiao, H., Valera-Medina, A., and Bowen, P. J. (2017a). Modeling Combustion of Ammonia/Hydrogen Fuel Blends under Gas Turbine Conditions. *Energy Fuels* 31 (8), 8631–8642. doi:10.1021/acs.energyfuels.7b00709

Xiao, H., Valera-Medina, A., and Bowen, P. J. (2017b). Study on Premixed Combustion Characteristics of Co-firing Ammonia/methane Fuels. *Energy* 140, 125–135. doi:10.1016/j.energy.2017.08.077

Xiao, H., Valera-Medina, A., Marsh, R., and Bowen, P. J. (2017c). Numerical Study Assessing Various Ammonia/methane Reaction Models for Use under Gas Turbine Conditions. *Fuel* 196, 344–351. doi:10.1016/j.fuel.2017.01.095

Xiao, H., Lai, S., Valera-Medina, A., Li, J., Liu, J., and Fu, H. (2020). Study on Counterflow Premixed Flames Using High Concentration Ammonia Mixed with Methane. *Fuel* 275, 117902. doi:10.1016/j.fuel.2020.117902

Xu, L., McCabe, R. W., and Hammerle, R. H. (2002). NO_x Self-Inhibition in Selective Catalytic Reduction with Urea (Ammonia) over a Cu-Zeolite Catalyst in Diesel Exhaust. *Appl. Catal. B: Environ.* 39, 51–63. doi:10.1016/s0926-3373(02)00074-7

Yang, G., Guo, H., Kang, Z., Zhao, L., Feng, S., Jiao, F., et al. (2019). Green Hydrogen Separation from Nitrogen by Mixed-Matrix Membranes Consisting of Nanosized Sodalite Crystals. *ChemSusChem* 12, 4529–4537. doi:10.1002/cssc.201802577

Yun, B. K., and Kim, M. Y. (2013). Modeling the Selective Catalytic Reduction of NO_x by Ammonia over a Vanadia-Based Catalyst from Heavy Duty Diesel Exhaust Gases. *Appl. Therm. Eng.* 50, 152–158. doi:10.1016/j.applthermaleng.2012.05.039

Zakaznov, V. F., Kursheva, L. A., and Fedina, Z. I. (1978). Determination of Normal Flame Velocity and Critical Diameter of Flame Extinction in Ammonia-Air Mixture. *Combust. Explos.* 14, 710–713.

Zamfirescu, C., and Dincer, I. (2008). Using Ammonia as a Sustainable Fuel. *J. Power Sourc.* 185, 459–465. doi:10.1016/j.jpowsour.2008.02.097

Zamfirescu, C., and Dincer, I. (2009). Ammonia as a green Fuel and Hydrogen Source for Vehicular Applications. *Fuel Process. Techn.* 90, 729–737. doi:10.1016/j.fuproc.2009.02.004

Zhang, M., Wei, X., Wang, J., Huang, Z., and Tan, H. (2020). The Blow-Off and Transient Characteristics of Co-firing Ammonia/methane Fuels in a Swirl Combustor. *Proc. Combust. Inst.* 38, 5181–5190. doi:10.1016/j.proci.2020.08.056

Zhang, M., An, Z., Wang, L., Wei, X., Jianayihan, B., Wang, J., et al. (2021a). The Regulation Effect of Methane and Hydrogen on the Emission Characteristics of Ammonia/air Combustion in a Model Combustor. *Int. J. Hydrogen Energ.* 46, 21013–21025. doi:10.1016/j.ijhydene.2021.03.210

Zhang, M., An, Z., Wei, X., Wang, J., Huang, Z., and Tan, H. (2021b). Emission Analysis of the CH_4/NH_3/air Co-firing Fuels in a Model Combustor. *Fuel* 291, 120135. doi:10.1016/j.fuel.2021.120135

Zhou, S., Yang, W., Tan, H., An, Q., Wang, J., Dai, H., et al. (2021). Experimental and Kinetic Modeling Study on NH_3/syngas/air and NH_3/bio-syngas/air

Premixed Laminar Flames at Elevated Temperature. *Combust. Flame* 233, 111594. doi:10.1016/j.combustflame.2021.111594

Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.