ANALYSIS OF AMMONIA FUEL APPLICATION TECHNOLOGY AND DEVELOPMENT PROSPECTS

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Abstract

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With the global trend towards carbon neutrality, the use of renewable energy and carbon-neutral fuels has become a key to achieving sustainability. Hydrogen is considered as the most ideal clean energy source. However, the high production cost, storage and transportation issues limit its large-scale promotion. Ammonia, as a zero-carbon alternative fuel, has high energy density, easy transportation and other advantages, which have attracted increasing attention from many researchers. Ammonia has the potential to be developed in different fields. However, it also met some challenges such as unstable combustion and high NO_x emissions. This thesis discusses the physical and chemical characteristics of ammonia fuels and presents applications of ammonia fuel in different fields. Furthermore, this thesis also provides an expectation for the prospects of the development of ammonia fuels.

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1 Introduction

The rational use of energy has always been a challenge for human society. With the global trend towards carbon neutrality, the imminent depletion of fossil fuels and the increasing degradation of the environment, the use of renewable energy sources and carbon-neutral fuels has become the key to achieve sustainable human development. The low-carbon transition therefore becomes a common choice in the energy strategies of many countries (Xiao et al., 2024).

Among most of alternative fuels such as ethanol, biofuels and waste-derived oils, hydrogen is more favored by the public due to its abundant, higher calorific value, and non-polluting advantages. It is considered to be the most ideal clean energy source (Pareek et al., 2020). Many studies suggest utilizing hydrogen as a synthetic fuel instead of fossil fuels and renewable energy sources (Zamfirescu & Dincer, 2009).

However, as the hydrogen economy develops further, its use as a fuel source still faces significant challenges. The volatile nature of hydrogen and its wide flammability limits present serious safety problems in distribution and storage (Yi et al., 2023). Moreover, its invisible flame leads to a potential explosion danger and hydrogen provides less energy per unit volume compared to conventional fuels used in transport vehicles (Chen et al., 2020). These are currently a barrier for its implementation. As a result, the limitations and dangers of hydrogen fuel have prevented it from being widely promoted, and people have had to start exploring other alternative fuels.

As a hydrogen-rich carrier, ammonia is gradually gaining attention due to it higher energy density, ease of storage and transport, and environment-friendly combustion products. Ammonia fuel has the potential to replace petrol, diesel and other fossil fuels in applications, providing a new way to solve problems such as environmental pollution.

There is sufficient technology to enable the development of ammonia fuels based on existing production and transport processes (Dimitriou & Javaid, 2020). In recent years, many countries have drawn great attention to ammonia, seeing it as the future direction of energy development. More and more researchers have also taken the development and application of ammonia fuel as a key research direction.

The goal of this thesis is to analyze the application of ammonia fuel and point out its development prospects. This thesis is presented in subsequent chapters, starting with an overview of ammonia properties and its production and transportation (Chapter 2), followed by an exploration of its applications in different fields (Chapter 3). Chapter 4 will analyze current issues

and offer insights into the future prospects of ammonia fuel. And Chapter 5 will summarize the findings and provide a comprehensive overview of the whole paper.

2 Ammonia

This section outlines the various properties of ammonia and the processes related to its production and transportation. It provides a clear and understandable overview of ammonia.

2.1 Physical and chemical properties of ammonia

Ammonia, an alkaline, is a colorless and easily liquefiable gas with distinctive odor under normal condition (at room temperature and pressure), which can solute in water (Dincer et al., 2023). Under normal conditions, the density of ammonia is 0.771 kg/m^3 which is lighter than air. Furthermore, it has a nature of fast diffuse, which means the consequences of leakage is relatively small (Dinçer & Siddiqui, 2020). The flammability limit of gaseous ammonia in air ranges from 15.5% to 27.0%, which compare to hydrogen (4.7% to 75.0%) makes transportation of ammonia a much safer option (Brandhorst et al., 2008).

Ammonia consists of a single nitrogen atom and three hydrogen atoms, and it has a stable polar structure (Dincer et al., 2023). It produces only nitrogen and water (as in Equation 1) when completely burned, making it a carbon-free fuel that is friendly to the environment.

$$4NH_3 + 3O_2 \rightleftharpoons 2N_2 + 6H_2O \tag{1}$$

Ammonia is a good hydrogen energy carrier. It contains 17.6% of hydrogen per unit mass, which is higher than that of methanol (12.5%) (Dinçer & Siddiqui, 2020). This content is also more than 1.5 times higher as liquid hydrogen and 9 times higher as lithium-ion batteries (Gao, Liu & Li, 2022). According to Lesmana et al. (2019) and Dincer et al. (2023), the energy density of ammonia and other fuels is shown in Table 1. It should be noticed that the formulas for gasoline and diesel are simplified here for a better understanding, whereas in reality they are complex mixtures of hydrocarbons.

Table 1: Comparison of the energy density of ammonia and other fuels.

Fuel	Formula	Energy density [GJ/m^3]
Ammonia	NH_3	11.2
Hydrogen (l)	H_2	8.5
Hydrogen (g)	H_2	2.1
Methane	CH_4	7.1
Ethanol	C_2H_6O	21.3
Gasoline	C_8H_{18}	31.3
Diesel	$C_{12}H_{23}$	36.5

*l: liquid, g: gaseous

As can be seen from the comparison, the energy density of ammonia is similar to natural gas and is much higher than hydrogen (both liquid and gaseous state). However, it is still small compared to conventional fuels.

2.2 Combustion characteristics

Ammonia has been widely used in many fields such as agriculture, transportation and refrigeration. In recent years, it has attracted further study by researchers and engineers due to its carbon-free properties. As a solution for hydrogen energy options and hydrogen economy challenges, ammonia can be used directly with the present infrastructure without any changes (Erdemir & Dincer, 2020).

Among those researches, the attempts to use ammonia in internal combustion engines and gas turbines have considerably increased, accounting for a large portion. Therefore, in order to better utilize ammonia fuels, it is necessary to get insight into the combustion properties of ammonia and compare them with other fuels.

According to Erdemir & Dincer (2020), and Lesmana et al. (2019), the most common fuels together with the ammonia's combustion characteristics are summarized in Table 2.

Table 2: Comparison of common fuels with ammonia.

	Ammonia	Hydrogen (l/g)	Gasoline	Diesel	CNG	Ethanol
Formula	NH_3	H_2	C_8H_{18}	$C_{12}H_{23}$	CH_4	C_2H_6O
Density/kg·m^{-3}	0.6	0.071	0.75	0.86	0.2	0.79
Energy density/MJ·L^{-1}	11.2	8.5/2.1	31.1	36.4	7.1	21.3
LHV/MJ·kg^{-1}	18.8	120.1	44.5	43.5	38.1	26.9
HHV/MJ·kg^{-1}	22.5	141.9	47.3	44.8	55.3	29.7
Boiling point/°C	-33	-253	33-190	>200	-161	78
Flame speed/m·s^{-1}	0.15	3.51	0.58	0.87	8.45	0.39
Flammability limits/Vol.%	16-25	4-75	1.4-7.6	0.6-5.5	5.0-15.0	3.3-19
Autoignition temperature/°C	651	585	248-412	226-233	450	363
Minimum ignition energy/MJ	8	0.02	0.2	0.2-0.3	0.285	0.65
Latent heat of vaporization/kJ·kg^{-1}	1370	445.6	305	270	504	840
Octane	>111	$\geq$ 120	92-98	-	107	108
Air-fuel ratio	6.06	34.3	14.6	14.5	17.2	9.0

*l: liquid, g: gaseous, CNG: Compressed natural gas, LHV: Lower heating value, HHV: Higher heating value

Based on the comparison listed in Table 2, it can be known that ammonia burns slowly and has a relatively low calorific value. Due to issue of self-ignition, it usually needs to be mixed with other fuels for combustion. The minimum ignition energy of ammonia is 8 MJ, which is significantly higher than other fuels. Moreover, ammonia has a high-octane number, making it more explosive-resistant.

2.3 Production, transport and storage

The most widely use of ammonia is as a feedstock for nitrogenous fertilizers in agriculture, and this demand is increasing annually (Berwal, Kumar & Khandelwal, 2021). Approximately 80% of the ammonia is used as a feedstock for chemical and fertilizer production, while only a small amount used for direct applications.

Today, the most mature process for ammonia production in industry is the Haber-Bosch process, which uses hydrogen and nitrogen to synthesize ammmonia at high temperatures and pressures (as in Equation 2).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \tag{2}$$

Since nitrogen makes up the majority of the atmosphere, it is available through a variety of technologies. Meanwhile, hydrogen can also be obtained through various methods, such as biomass gasification and electrolysis. The gasification of biomass is a relatively mature technology that use heat, steam, and oxygen to convert biomass to hydrogen and other products (Energy, 2019). On the other hand, electrolysis, which is a well-known technology for hydrogen production, is the process of using electricity to split water into hydrogen and oxygen (Shiva Kumar & Lim, 2022). These technologies can achieve nearly carbon-free production. However, large-scale hydrogen production still needs to rely on fossil fuels, as the methods mentioned above increase the cost of ammonia production at the same time. (Dincer et al., 2023)

According to the research by Gao et al. (2022), the process of steam reforming used in Haber-Bosch process involves three main technologies in terms of water-gas shift reaction, separation and purification. The majority of greenhouse gases are released during methane-steam reaction and water-gas shift, making hydrogen production the main source of CO_2 emissions in the Haber-Bosch process.

Globally, Haber-Bosch is the most commonly used ammonia production process that has been in use since 1913. As efficiency of a single conversion pass of ammonia can reach about 15%, no other method could compare to the Haber-Bosch process (Lyon, 2017). Based on efficiency and cost, efforts for the development of new ammonia production methods and improvement of the conventional system are still in progress.

In most cases, ammonia is stored and transported as a liquid, and two methods are commonly used: pressurized storage and cooled storage. In addition, ammonia storage is more

economical, and infrastructure of propane storage and transportation can also be used for liquid ammonia (Xu et al., 2022). However, ammonia is a corrosion hazard for some metals such as copper, copper alloys, and nickel alloys with concentrations greater than 6%, so stainless steel or carbon fiber tanks and piping with polyethylene liners need to be replaced for use (Duijm, Markert & Paulsen, 2005).

In order to improve the safety of ammonia storage, researchers are also developing new technologies. For example, the use of metal ammonium complexes like $Mg(NH_3)_6Cl_2$, which can be safely and efficiently handled as a source of ammonia using its thermal decomposition process (as in Equation 3) (Xu et al., 2022).

$$Mg(NH_3)_6Cl_2(s) \rightleftharpoons 4NH_3(g) + Mg(NH_3)_2Cl_2(s) \tag{3}$$

In addition, according to the research Godfrey et al. (2018), the porous metal-organic framework MFM-300 (Al) also has the potential to be a portable ammonia storage material with excellent adsorption capacity.

2.4 Comparison between ammonia fuel and other fuels

Taking into account all the properties of ammonia, some of the notable benefits of it can be summarized as follows:

- Compared to hydrogen, ammonia has a higher energy density and a narrower flammability limit, which means it is advantageous in terms of storage and transportation and also safer to use as a fuel than hydrogen.
- Ammonia has a lower LHV than other fuels, but a higher-octane number, which provides better resistance to explosion.
- In its liquefied state, it contains about 48% more hydrogen per volume than hydrogen gas.
- The product of complete combustion is carbon-free and environmentally friendly. Due to its distinctive odor, it can be easily detected when spillage.
- Ammonia has low vapor pressure and low boiling point compared to many hydrocarbon fuels like gasoline and diesel, making it feasible to store and transport in its liquid state at relatively low temperatures and pressures.

Meanwhile, it has some disadvantages:

- The latent heat of vapor value of ammonia is 1370 kJ/kg. This high value indicates that

ammonia can absorb a lot of heat during phase change, leading to a lower combustion temperature.

- Ammonia has a narrow flammability limit, which can lead to fire under certain conditions.
- Flame speed of ammonia is very slow, while other fuels can burn twice as fast and even faster. Using ammonia as a fuel is likely to have incomplete combustion and low efficiency.
- Ammonia has large minimum ignition energy values, requiring more energy compared to other fuels. Meanwhile, it has a high ignition temperature of 651°C, which means it is difficult to be ignited.

It can be seen that the use of ammonia as a fuel has some advantages over conventional fuels such as hydrogen, gasoline and diesel. At the same time, however, ammonia has a number of properties that affect its competitiveness.

3 Applications

In this chapter, various applications of ammonia fuel will be presented one by one, including its use in gas turbines, internal combustion engines, fuel cells and marine fuel. It offers a better understanding of the application of ammonia fuels.

3.1 Gas turbines

Gas turbines are commonly used in power plants and most of them are large-scale turbines with a wide power range. Using natural gas as fuel is the common choice of most existing power plants (Pashchenko, 2024).

According to Valera-Medina et al. (2018), research on the combustion systems of gas turbines using ammonia as a fuel has been conducted since the 1960s. Solar and UC Berkeley conducted research on a 250 HP T-350 gas turbine in the United States. They found that the power of a gas turbine using ammonia can increase by 10% to 20% when the inlet temperature of the turbine matches that of hydrocarbons. It can also achieve considerably higher efficiency. This research not only investigated the combustion characteristics of ammonia but also identified the basic issue that ammonia has a relatively low reaction rate in further studies. Therefore, the same group of researchers proposed that 28% of dissociated ammonia can be used as an alternative fuel for hydrocarbon-fueled gas turbine systems.

During the 1990s and 2000s, a variety of studies have focused on the combination of ammonia and other fuels that can be used in gas turbines, which furthers the development of ammonia fuels (Pashchenko, 2024). However, the major limited factors of NO_x emissions and combustion efficiency were recognized as the usage of ammonia fuels in gas turbines increased. SPG Advanced Propulsion and Energy summarized the main challenges to develop a reliable ammonia combustion technology (Xu et al., 2022).

- Lower temperature tempering properties of flame and slower rate of kinetics
- Unstable combustion
- Efficiency improvement requires a good evaporation rate
- Fuel cracking is necessary to increase the flame speed and combustion rate

Meyer et al. (2011) analyzed swirl stabilized combustion of ammonia with other molecules at the University of Iowa. The study found that the use of swirlers can make the combustion of ammonia and other fuels with different concentrations stable. Additionally, the use of a flame holder can increase the combustion efficiency with a significant reduction in NO_x emissions. Meanwhile, researchers at the National Institute of Advanced Industrial Science

and Technology (AIST) in Japan have developed a micro-gas turbine with extremely low NO_x emission (Iki et al., 2016). They tested different combustion chambers under different operating conditions.

As a promising fuel that can reduce CO_2 emissions, the application of ammonia fuel in this field is still in an early stage of development. Since the technology is immature, there are only a few gas turbines that run on ammonia in use around the world. However, there are also some development were made. In 2020, Mitsubishi Power designed a 40 MW gas turbine based on their H-25 series (as in Figure 1), which can combust 100% ammonia (POWER, 2021).

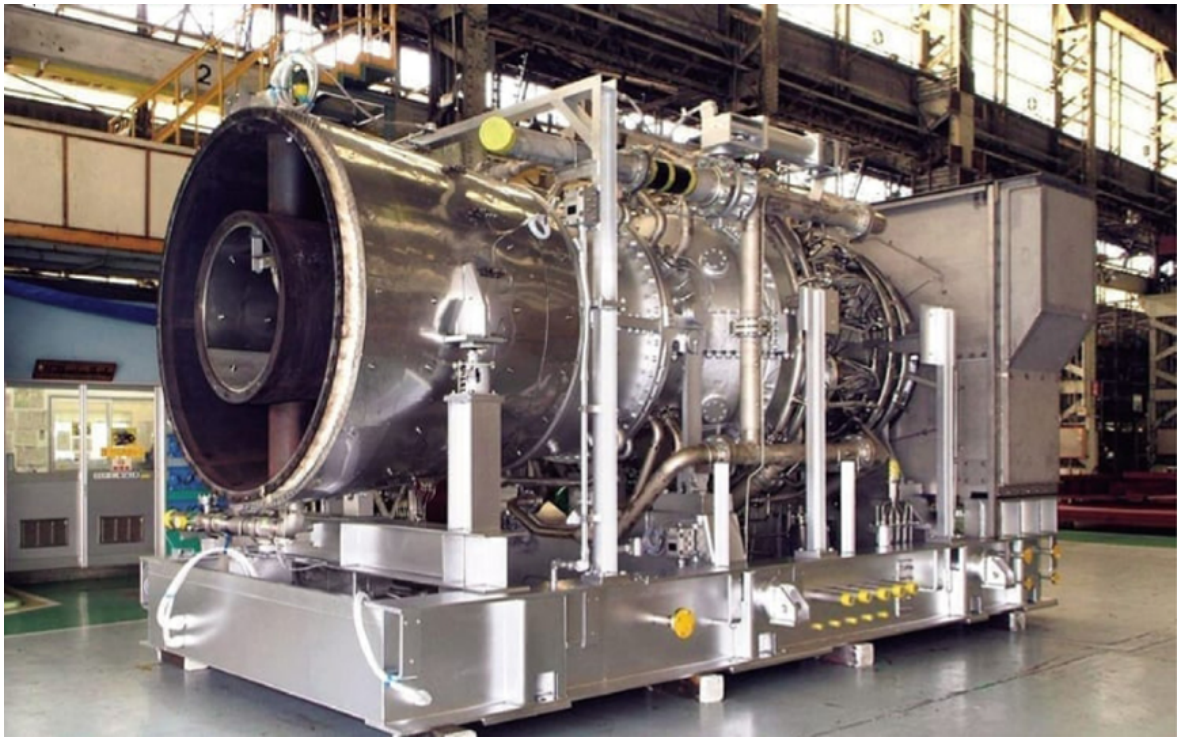

Figure 1: Ammonia-fired gas turbine (H-25 series) (POWER, 2021)

According to Noble et al. (2021), Siemens from Germany developed an ammonia-fired gas turbine. It is now being tested in Sweden. Turboden from Italy installed a gas turbine that can operate on only ammonia or a mixture of ammonia and natural gas in a cogeneration plant in Germany (Singh & Pedersen, 2016); Kawasaki Heavy Industries developed a 1 MW ammonia-fired gas turbine, which is currently being tested in Japan (Pashchenko, 2024).

Using ammonia fuels in the field of gas turbines is a promising new technology in this world. However, its performance and efficiency data is limited. Lots of experts believe that ammonia will play an important role in the transition to a low-carbon energy system (Pashchenko, 2024), with promising results from tests and pilot projects.

3.2 Internal combustion engines

The internal combustion engine is the most commonly used power source for road traffic and defense equipment in the world today. Internal combustion engines work by burning a mixture of fuel and air inside a combustion chamber to create controlled explosions. These explosions generate the power needed to drive the vehicle forward.

While there are newer technologies emerging, such as electric vehicles, the internal combustion engine remains popular due to its reliability, efficiency, and affordability. According to the study by Xu et al. (2022), the first application of ammonia to a small locomotive engine was developed as early as 1882. In the middle of the 1960s, more and more researchers began to conduct further research on the application of ammonia as a fuel for internal combustion engines.

Internal combustion engines can be classified into spark ignition (SI) engines and compression ignition (CI) engines by their different ignition type. According to Cardoso et al. (2021), ammonia can be used as a fuel for these two engines in three different ways:

- Pure ammonia fuel
- Blending with hydrocarbon fuels
- Blending with hydrogen

However, they all have their defects. The combustion of pure ammonia is really challenging due to its poor combustion characteristics. It can reduce about 20% of the output power of an SI engine (Cardoso et al., 2021). Blends of ammonia and hydrocarbon fuels result in significant NO_x, CO and unburnt hydrocarbon emissions (Ryu, Zacharakis-Jutz & Kong, 2014). In addition to the storage issue, hydrogen has the possibility of damaging the engine systems because of its easy-diffuse property (Nash et al., 2012).

To better utilize ammonia as a fuel for internal combustion engines, improvements are necessary in order to obtain more ideal performance. Numerous efforts and experiments have been made for this purpose. Comotti & Frigo (2015) designed a new production system for hydrogen that used ammonia as a feedstock. The hydrogen produced by the decomposition of ammonia is then mixed with ammonia and combusted in the engine. This study found that this system can provide enough hydrogen for combustion with good engine performance.

Lee & Song (2018) developed a combustion strategy for an internal combustion engine using only ammonia as a fuel. They found that internal combustion engines need extremely high compression ratios so that they can reach a sufficient temperature. Mounaïm-Rousselle

& Brequigny (2020) showed that the use of pure ammonia as a fuel for internal combustion engines is feasible under certain conditions, as long as its combustion stability can be maintained.

3.2.1 Compression ignition engines (CI)

Compression ignition engine engines are used in a variety of applications including cars, ships and power generation. The work cycle of four stoked-engine is showed as in Figure 2. The heat is generated through mechanical compression within the cylinder to ignite the injected fuel.

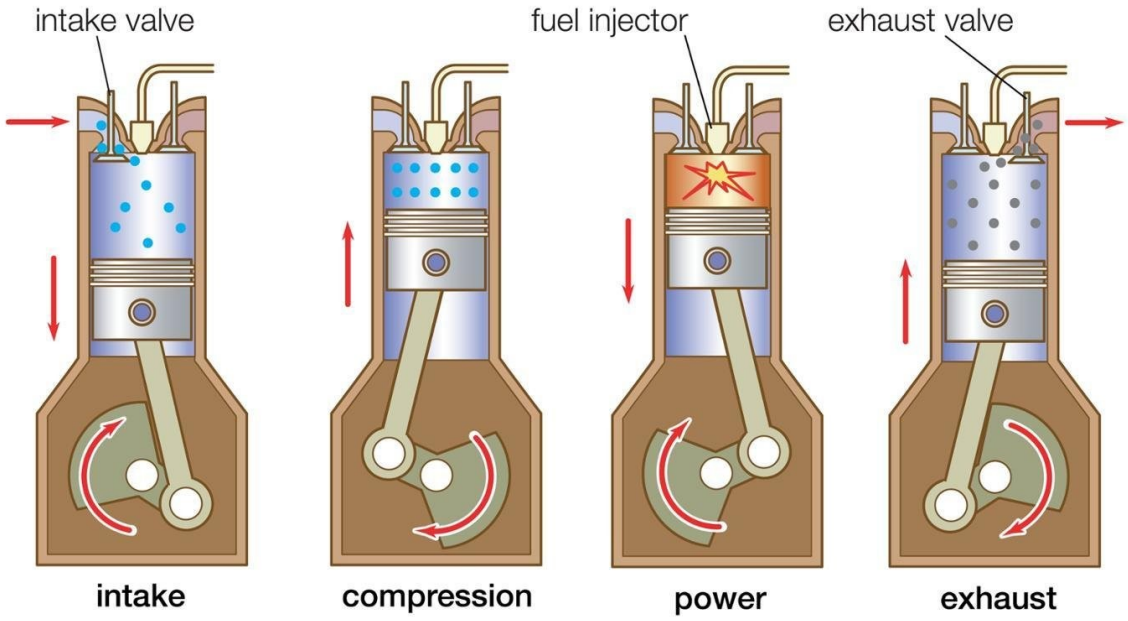

Figure 2: Operation of four-stroke CI cycle (Baechtel, 2018)

Ammonia-hydrocarbon dual-fuel operation

According to the research by Dimitriou & Javaid (2020), the pure ammonia fuel used in CI engines is limited, and its implementation is still a challenge. However, ammonia is still considered a suitable alternative to some fuels, such as diesel, bio-diesel or dimethyl ether (DME) for blending purposes. Ammonia-diesel was one of the first fuels to be tested as an ignition source in 1996. The study found that this blend of fuel can make a CI engine have a lower compression ratio of 15.2:1 compared to a pure ammonia fueled engine (Dimitriou & Javaid, 2020). This finding contributed to further research related to this field.

Reiter & Kong (2011) demonstrated the operation of a CI engine with ammonia in dual-fuel mode. They determined the feasibility of the ammonia-diesel or ammonia-biodiesel system, suggesting that the amount of diesel in use should be between 40% and 60% in

order to achieve the best performance. Furthermore, researchers also tested the combustion of ammonia blended with other fuels, such as gasoline and ethanol. They found that these blended fuels could provide a high power output under stable conditions. However, they were still affected by the production of byproduct NO_x in the real combustion process.

Ammonia-hydrogen dual-fuel operation

Pochet et al. (2017) conducted research on the operation of an ammonia-hydrogen fueled homogeneous charge compression ignition (HCCI) engine. They recommended using higher compression ratios and intake pressures when using ammonia. It could help reduce the need for intake gas heating and increase the engine efficiency. This highlights the benefit of variable compression ratio (VCR) engines in offering a greater hydrogen-ammonia mixing ratio, leading to longer combustion durations.

Ammonia-diesel or ammonia-biodiesel blending fuels have been efficiently demonstrated for their usage in CI engines. However, there is limited research on ammonia blended with other fuels, such as hydrogen, and there are few relevant comparisons available.

3.2.2 Spark ignition engines (SI)

Spark ignition engines are used worldwide in power units with small bore cylinders such as vehicles. The work cycle of a four stoked-engine is showed as in Figure 3. The heat is generated through the ignition of the air-fuel mixture with the help of a spark plug.

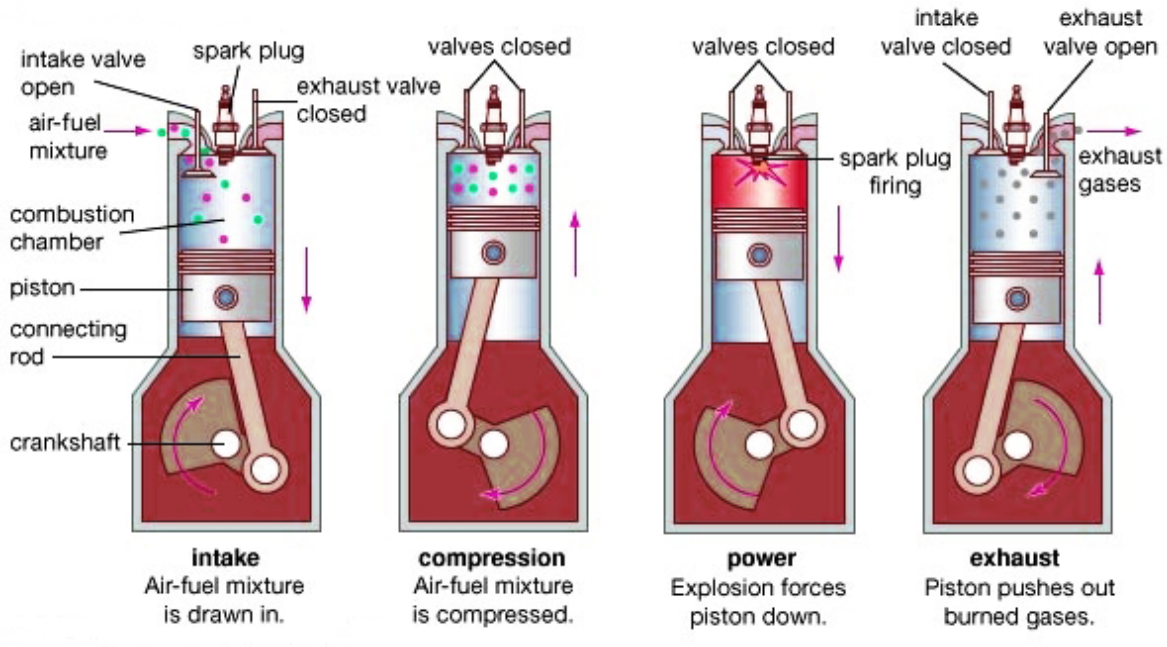

Figure 3: Operation of four-stroke SI cycle (Mechdiploma, 2020)

Ammonia-hydrocarbon dual-fuel operation

According to the research by Grannell et al. (2008), the suggested compression ratio for an ammonia-gasoline engine is 10. When the effective pressure is greater than 400 kPa, ammonia can replace most gasoline in a SI engine. However, the ratio of ammonia to gasoline has to be adjusted based on the load. Guo et al. (2022) discovered that in the ammonia-gasoline system under a lean combustion condition, the increase in the portion of ammonia results in decreased combustion speed, which results in a longer combustion duration.

Moreover, Oh et al. (2021) tried to blend ammonia with methane to investigate its potential as a dual-fuel for SI engines. The findings indicated a significant reduction in CO_2 emissions, but the output power declined gradually with the increase in ammonia. The performance of an ammonia-methane fueled engine was disappointing.

Ammonia-hydrogen dual-fuel operation

Ammonia-hydrogen blended fuel has been considered as the most suitable and ideal fuel for SI engines (Liu, Wu & Wang, 2022). Several studies have been conducted to determine the optimal efficiency using different ratios of ammonia and hydrogen. Mounaïm-Rousselle et al. (2021) showed that the engine can operate stably with a hydrogen volume of 10%. In the Lhuillier et al. (2020) study, it was noted that a small portion of hydrogen can help improve engine performance and stability. However, as the percentage of hydrogen increases, heat loss from the engine's inner wall also increases.

In addition, Koike & Suzuoki (2019) found that the ratio of ammonia to hydrogen in the fuel also determines the flame speed. They highlighted that ammonia and hydrogen have to meet a ratio of 3:2 in order to match the same combustion duration as a gasoline combustion engine. However, this would also lead to a significant loss of energy, such as heat loss.

Most recent research has focused on the operation of ammonia-hydrogen blended fuel in SI engines and obtained notable progress. Hydrogen has a high calorific value and is a cleaner fuel compared to gasoline and methane. However, it still presents some challenges in terms of production and storage.

3.3 Fuel cells

Fuel cells are another application of ammonia fuel, which allow the production of electrical energy directly from the chemical energy of a fuel. Ammonia fuel cells can be classified into indirect ammonia fuel cells (IAFC) and direct ammonia fuel cells (DAFC) by their different ways of providing ammonia. Indirect ammonia fuel cells need an external dissociation unit

to produce hydrogen for the cell, and ammonia here will be treated as a means of hydrogen storage (Dinçer & Siddiqui, 2020). On the other hand, direct ammonia fuel cells can input ammonia fuel directly without any external dissociation.

Direct ammonia fuel cells can be further divided into four types according to different electrolytes. They are oxygen anion conducting solid oxide fuel cells (SOFC-O), proton anion conducting solid oxide fuel cells (SOFC-H), proton exchange membrane fuel cells (PEMFC) and alkaline membrane fuel cells (AMFC). Solid oxide fuel cells are the most commonly studied type, and they have excellent performance in terms of flexibility, energy efficiency and emissions (Li et al., 2023). It is also a promising fuel cell that can be applied to marine applications.

3.3.1 Oxygen anion conducting solid oxide fuel cells

The work principle of oxygen anion conducting solid oxide fuel cells is based on the transportation of oxygen ions from the cathode to the anode, where they react with hydrogen to produce water and release electrons (Wang et al., 2022). Figure 4 shows the working principle of SOFC-O.

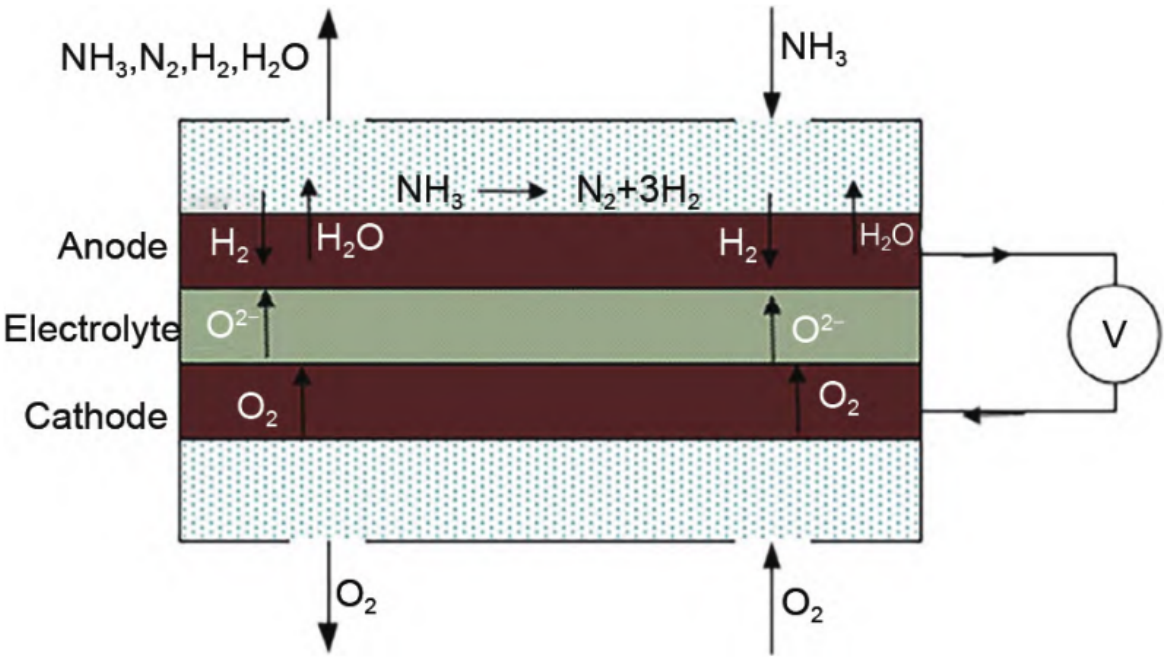

Figure 4: Working principle of SOFC-O (Chen & Liu, 2023)

According to Ni et al. (2023), the earliest study was conducted using yttria-stabilized zirconia (YSZ) in 1980. It was found that the nitrogen oxide produced at the anode can reach a yield of 60%. Subsequently, Wojcik et al. (2003) conducted the first systematic study on solid oxide fuel cells fueled with ammonia and modified the anode material based on previous

study. The researchers discovered that the combination use of YSZ, platinum electrodes and an iron catalyst can reach a peak power density of 50 $mWcm^{-3}$ at 800 °C. This study contributed to the extensively studies of SOFC-O using different electrodes and electrolytes (Dinçer & Siddiqui, 2020).

Stoeckl et al. (2019) investigated how flow rate and fuel pressure affect the power density of the cell. They used a YSZ electrolyte, a Ni-YSZ anode, and a Lanthanum Strontium Cobalt Ferrite (LSCF) cathode. This study noted that a proper increase in flow rate can improve cell power. However, an excessive increase in flow rate may lead to a decline in the decomposition rate of ammonia. Shy, Hsieh & Chang (2018) developed a pressurized SOFC using a YSZ electrolyte, a Ni-YSZ anode and a cathode made of lanthanum strontium chromium-gadolinium-doped ceria (LSC-GDC). It was found that pressurization can greatly reduce the gas diffusion resistance, and the development of pressurized ammonia-fueled SOFC hybrids with micro-gas turbines is promising.

3.3.2 Proton anion conducting solid oxide fuel cells

The work principle of proton anion conducting solid oxide fuel cells is based on the transportation of positively charged protons (H^+) through the electrolyte. These types of fuel cells are high-temperature fuel cells that involve the dissociation of ammonia (Wang et al., 2022). Figure 5 shows the working principle of SOFC-H.

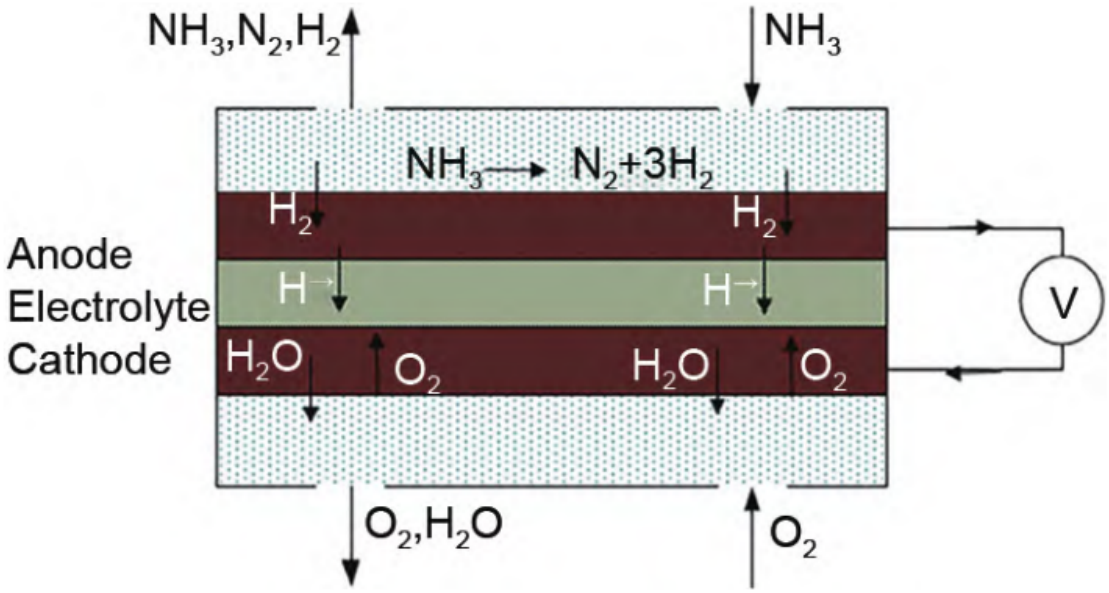

Figure 5: Working principle of SOFC-H (Chen & Liu, 2023)

SOFC-H has more advantages compared to SOFC-O as follows:

- There is no secondary reaction that generates NO_x on the anode side.

- The reaction product (water) is produced on the cathode side so that ammonia on the anode will not be diluted (Ishak, Dincer & Zamfirescu, 2012)
- The peak power density is about 20% to 30% greater than that of SOFC-O. Moreover, the utilization of ammonia can be improved (Ishak, Dincer & Zamfirescu, 2012)
- Plasmonic-based conductors have better conductive performance at low temperatures, leading to a decrease in the operating temperature of SOFCs (Ni et al., 2023)

Currently, perovskite is the most commonly used electrolyte and $BaCeO^{3-}$ based materials are the most widely studied (Wang et al., 2022). According to Lv et al. (2008) and Bhide & Virkar (1999), $BaCeO^{3-}$ based materials have poor stability in conditions containing water. To improve their stability and conductivity in practice, they are usually doped with ions such as Gd^{3+}, Y^{3+}, Eu^{3+}, Nd^{3+}, and Yb^{3+}.

Lots of researchers have developed various electrolytes based on the findings from previous studies. They achieved different results at peak power and kept making progress. Pelletier, McFarlan & Maffei conducted two studies through two electrolytes they developed, $BaCe_{0.8}Gd_{0.19}Pr_{0.01}O_{3-\delta}$ (BCGP) and $BaCe_{0.85}Eu_{0.15}O_3$ (BCE) in 2005 and 2008, respectively. The results showed that both cells had poor peak power at 600 °C and 700 °C, which were 28 $mWcm^{-2}$ and 35 $mWcm^{-2}$ respectively. However, Zhang & Yang (2008) used BCGP as electrolytes under different conditions and obtained a greater peak power of 147 $mWcm^{-2}$ at 600 °C.

Subsequently, research that aimed to optimize the performance of the cell was conducted in further studies. Lin et al. (2010) combined Zr and Y with $BaCeO^{3-}$ electrolytes, and obtained the results of peak power of 390 $mWcm^{-2}$ at 750 °C. Miyazaki et al. (2020) used $Ni-BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-d}$ (BCZY) as anode and $BaCe_{0.8}Y_{0.2}O_{2.9}$ (BCY20) as electrolytes for the tests. The study obtained a good result that peak power of 130 $mWcm^{-2}$ and 340 $mWcm^{-2}$ can be reached at 550 °C and 700 °C respectively.

3.4 Co-combustion in boilers

Coal remains the largest energy source for electricity generation, maintaining an important role in the world economy (IEA, 2023). However, the large amount of coal consumption brings serious carbon emissions, which accounted for 46.9% of global CO_2 emissions in 2020 (Kim et al., 2023b). In order to meet international climate targets, the NH_3 co-combustion in coal-fired power plants has been proposed to reduce emissions (Chen, Wang & Wang, 2023).

Numerous research have been conducted on the numerical modelling of characteristics of co-

combustion. IHI Corporation used different dimensional simulations and a 10 MW facility to study the problems related to ammonia-coal combustion (Ishii et al., 2020). Their results show that if appropriate injection method of ammonia can be used, 20% of NH_3 blended in the fuel could cause lower NO_x emissions than combusting using pure coal. Moreover, zero concentrations of ammonia at the inlet means the supplied NH_3 is almost completely burned during the process (Tan et al., 2023).

Zhang et al. (2020) investigated combustion process in a 8.5 MW facility and found that when using 10% of NH_3 blended fuel, which shows a most intense combustion, the quantity of unburned carbon is the least in the fly ash. However, the NO_x concentration in the flue gas reaches a maximum value. The research conducted by Ishihara, Zhang & Ito (2020) noted that NO_x emission increases monotonically with the increase of ammonia content at 20%-60% ammonia blending ratio, and decreases when the blending ratio continues to increase.

In addition to combustion characteristics, the injection methods of ammonia has been the focus of research. Tamura et al. (2020) evaluated three different ammonia injection methods using a facility of 1.2 MW capacity. It was found that when using nozzle with diameter of 6.4 mm and opening angle of 40°, NO_x emissions comparable to those from pure coal combustion can be achieved, even with an ammonia mixing ratio of 35%. According to Kobayashi et al. (2019), the Central Research Institute of Electric Power Industry (CRIEPI) explored the effect of the ammonia injection location on the NO_x emissions using a 760 kW test furnace with the setup shown in Figure 6. It was noted that there was no significant increase in NO_x emissions when ammonia was injected at 1 m from the sidewall compared to pure coal combustion, whereas the concentration of NO_x became higher as the injection position was shifted lower.

Previous studies on ammonia co-combustion have mainly focused on numerical simulations and improving the reactivity of ammonia combustion while reducing the NO_x generation (Kim et al., 2023a). In order to further promote co-combustion of ammonia, an increasing number of studies have been carried out in recent years on its effect on heat transfer within coal-fired boilers.

Zhang et al. (2020) noted that as the proportion of ammonia content in the fuel increases, the reduction of particle radiation leads to a decrease in radioactive heat transfer in the furnace and a slight increase in convective heat transfer. Similar conclusions were obtained by Lyu et al. (2023) in a 600 MW coal-fired boiler. They also suggested that the temperature in the furnace could be raised by increasing the oxygen content to increase the radioactive heat transfer. In addition, Kim et al. (2023a) studied radioactive and convective heat transfer with the reduction in flue gas flow rate. And it was found that higher coal grades can reduce the

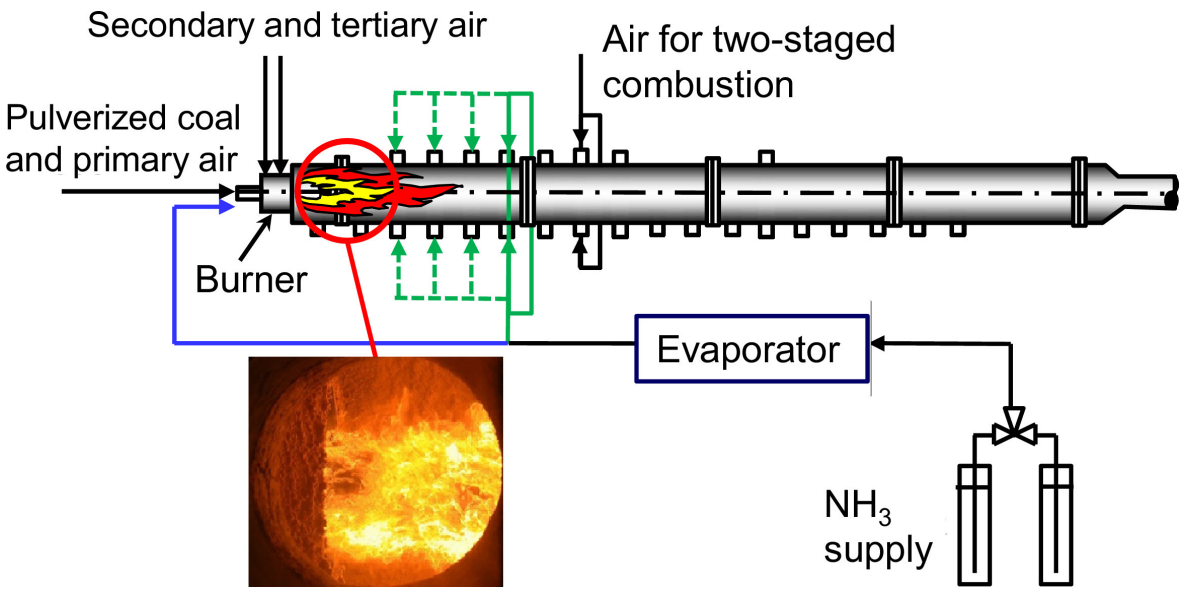

Figure 6: Horizontal test furnace combustion with ammonia (Kobayashi et al., 2019)

temperature of main and reheat steam more during ammonia co-firing. This suggests that the ammonia co-combustion strategy was beneficial for CFB boilers using lower coal grades.

IHI Corporation from Japan has made significant attempts in this field, and has recently entered the demonstration project stage with the support of preliminary basic tests and simulation data (Gao et al., 2022). In order to further promote the use of ammonia-coal combustion, the combustion characteristics of ammonia in different coal-fired facilities need to be focused on, and the relevant basic research, pilot tests and industrial demonstration studies need to be carried out urgently.

3.5 Marine fuel

Ammonia has been one of the most promising alternative fuels for marine ships in recent years. SOFC and internal combustion engines are both relevant to this field, and several marine engine manufacturers have actively supported the use of ammonia fuel. MAN B&W announced that its LPG-fueled engine would work on ammonia within 2-3 years (Laursen & Solutions, 2018). Wartsila has focused on modifying engines to use ammonia as a fuel in 2019 (Zincir, 2020). Moreover, ABS released a white paper in 2018 that investigated the restricted factors associated with the use of ammonia as a marine fuel (Bai, 2021). This paper evaluated the design as well as the operational challenges faced by ammonia-fueled ships. It provides shipowners with a good insight into using ammonia as a marine fuel and helps them evaluate it as an option in both the short and long run.

The marine industry is expanding research on ammonia-fueled ships as a consequence of the

growing recognition of ammonia's benefits as a marine fuel. A number of manufacturers have collaborated on projects and received Approval in Principle (AIP), promoting greater usage of ammonia fuel. Wärtsilä cooperated with Knutsen OAS Shipping AS, Repsol and the Sustainable Energy Catapult Centre to test a large-scale ammonia-fueled marine with a four-stroke combustion engine (ABS, 2020). This project started during the first quarter of 2021 in the Sustainable Energy Catapult Center at Stord, Norway. Meanwhile, a joint study by ABS, Nanyang Technological University and the Ammonia Safety and Training Institute was carried out in 2021 to explore the potential for ammonia as a marine fuel (ABS, 2021). This study highlighted the importance of ammonia in helping decarbonize the marine industry.

According to Wang (2021), MAN Energy Solutions and the Shanghai Merchant Ship Design & Research Institute (SDARI) have designed and developed an ammonia-fueled low-emission feeder container vessel. This joint project aimed to produce designs for an ammonia-fueled Chittagongmax container carrier with a 2700 TEU capacity.

> "Ammonia is an energy source with significant potential to help the industry meet IMO 2030 and 2050 emission targets but will require stringent new safety standards to be developed in order to support its adoption," said Dr. Xiaozhi (Christina) Wang, ABS Vice President, Global Marine. "This innovative project is typical of how ABS is working with leading partners across the world to support the development of next generation fuel solutions for shipping." (ABS, 2019)

MAN Energy Solutions also collaborated with Daewoo Shipbuilding & Marine Engineering (DSME) to design a 23000 TEU ammonia-fueled container ship. As expected from MAN, this ship can be delivered in 2024 and be in commercial operation by 2025 (SHIPPING-WATCH, 2020). Furthermore, Mitsui O.S.K. Lines cooperated with ITOCHU Corporation, Royal Vopak and other six partners to develop a supply network for ammonia-fueled ships in Singapore (POWER, 2021). They aimed to increase the production of ammonia fuel to meet the requirements of the marine industry and pave the path for future utilization of ammonia as a marine fuel.

The progress of using ammonia as an alternative to marine fuel depends mainly on the participation of industry manufacturers and joint research projects. The use of ammonia as a fuel in the marine industry indicates that the transition of the worldwide shipping sector is toward a more sustainable future. According to the World Energy Outlook 2022 released by the International Energy Agency (IEA, 2022), ammonia will meet around 45% of demand for shipping fuel by 2050. It is expected that over 60% of potential ships will be fueled

by ammonia or hydrogen by 2060. In addition, a lot of studies consistently have the same prediction that ammonia will be one of the main marine fuels in the future (Machaj et al., 2022).

4 Development prospect of ammonia fuel

This chapter outlines the challenges faced by ammonia fuels and the prospects for their future development.

4.1 Challenges of ammonia fuel

Low activity

Ammonia has poor combustion characteristics, and thus its reliability is still questionable. The main problems of ammonia include high ignition temperatures, low flame velocity and slow chemical kinetics. Due to these problems, using ammonia in IC engines is problematic at low loads and high engine speeds. Currently, there is no 100% ammonia engine for road transportation in the world. (El-Adawy, Nemitallah & Abdelhafez, 2024)

Some solutions have been proposed that use modified ammonia engines to replace or adapt existing gasoline or diesel engines. Investigations are currently being conducted to implement these types of technologies, and the main objective of them is to adapt ammonia fuels (Dinçer & Siddiqui, 2020). Furthermore, the air-fuel ratio of ammonia-fueled engines also needs to be modified compared to conventional engines due to the different air intake ratios.

Currently, the most possible method to use ammonia as fuel in IC engines is to blend it with other more reactive fuels such as gasoline, diesel, ethanol, methanol, hydrogen, etc. This is an effective way for existing internal combustion engines and gas turbines to shift from fossil fuels to carbon-neutral fuels (Chen & Liu, 2023). Common measures that can be taken also include raising the initial combustion temperature and conducting combustion in oxygen-enriched conditions (Xu et al., 2022). These methods can help to improve the low exothermic rate, stabilize the flame and improve the combustion efficiency of pure ammonia fuels (Xu et al., 2022).

NO_x emissions

The development of combustion technology using ammonia fuels has great potential. However, reducing NO_x and unburned ammonia is still challenging for further research and technologies (Valera-Medina et al., 2018). Ammonia is a carbon-free compound, so under a complete combustion state, it can only produce H_2O and N_2. However, the ideal combustion condition is hard to approach in reality, which means the combustion may increase the emissions of NO_x. While combusting ammonia blending fuels, CO_2 emissions can be increased at the same time. Furthermore, the portion of unburned ammonia in the flue gas may also

increase as the combustion temperature is low.

Exhaust Gas Recirculation (EGR) and Selective Catalytic Reduction (SCR) are two common methods to reduce the emission of flue gases (Helminen, 2021). According to Valera-Medina et al. (2018), EGR can considerably reduce NO_x emissions as a result of less oxygen usage. However, it was noted that the production of N_2O increases below a temperature of 1400 K. SCR is another effective way that can be employed to reduce these emissions (Niki et al., 2016). The work principal of it is using chemicals to decompose ammonia as equations 4, 5 and 6 shows (Valera-Medina et al., 2018).

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \tag{4}$$

$$2NO_2 + 4NH_3 + O_2 \longrightarrow 3N_2 + 6H_2O \tag{5}$$

$$NO_2 + NO + 2NH_3 \longrightarrow 2N_2 + 3H_2O \tag{6}$$

Currently, the control of NO_x emissions remains the main challenge for using ammonia as a fuel, which greatly limits its widespread usage. Future studies of applying ammonia fuels should focus on the evaluation of mechanisms of NO_x generation in flue gas, the treatment of emissions, and the analysis of flue gas characteristics from different engines. Meanwhile, it is also important to improve the reliability of existing ammonia combustion technologies, make them operate efficiently in different conditions.

Safety

Using ammonia as fuel is promising to help the decarbonization process. However, the flammability, toxicity and corrosiveness of ammonia cause safety issues. Ammonia may result in acutely dangerous effects in both humans and animals at certain doses. Additionally, it can cause intense irritation to the eyes, respiratory system, and skin tissues. Based on NFPA 704, ammonia was classified as a fuel that can cause serious or permanent injury (Machaj et al., 2022). Figure 6 shows the hazard classification and labelling based on the Classification, Labelling and Packaging (CLP) Regulation.

According to the hazard statements of CLP, ammonia causes severe skin burns and eye damage, is toxic if inhaled, is very toxic to aquatic life and is a flammable gas. Therefore, ensuring the safety of individuals and the aquatic environment is important when transporting ammonia as bunker fuel or other fuel carriers. The Nature and Biodiversity Conservation Union (NABU) also noted that strict safety regulations are needed to prevent ammonia leaks. Furthermore, use silicon-controlled catalytic converters to reduce NO_x emissions.

(SAFETY4SEA, 2021)

Figure 7: Hazard classification and labelling of ammonia (ECHA, 2023)

Besides toxicity and corrosiveness, ammonia also has the potential to cause explosion. According to Gao, Liu & Li (2022), ammonia is flammable at concentrations of 15% to 28% by volume in the air. It is a fire hazard, which can explode if released in an enclosed space with a source of ignition present. Additionally, there is a similar risk of explosions in ammonia storage tanks, and safety incidents may happen if leaks occur during the preparation and transportation process.

4.2 Potential opportunities

The application of ammonia brings significant economic and environmental benefits to the transportation sector as it is a zero-carbon fuel. According to the forecasts by Dincer et al. (2023), the usage of ammonia as a fuel will increase exponentially and there are still many uncertainties about the future of ammonia. However, ammonia as a fuel is effective and deserves further investigation.

In terms of reducing emissions, if ammonia synthesis utilizes energy and feedstock from renewable sources, it can achieve carbon neutrality over its entire life cycle (Xia et al., 2022). This is an important topic in the field of ammonia fuels and there have been studies in this area. For example, Rollinson et al. (2011) noted in their study that sustainable urea could be a promising source to provide ammonia for a wide range of industrial applications.

Many research institutes and companies have indicated their intentions to implement future projects on developing gas turbines powered by ammonia fuels. There has also been a proposal to use fuel cells and gas turbines together. Furthermore, Siemens predicted that the development of ammonia combustion technologies could lead the world toward a new era of renewable energy. (Dinçer & Siddiqui, 2020)

Moreover, ongoing research is focused on understanding the combustion mechanisms of pure ammonia fuels and ammonia blended with other fuels specifically in internal combustion

engines. Accelerating the development of various blended combustion systems to stabilize the ammonia combustion process is a promising direction for future research. An internal combustion engine powered by ammonia-hydrogen fuel has the potential to be a competitive zero-carbon power (Chen & Liu, 2023).

In the field of fuel cells, the use of ammonia plays an important role in the development of carbon-free energy. Currently, further studies in order to improve the performance of ammonia fuel cells are required. It is a challenge to create catalysts that are compatible with ammonia. Moreover, obtaining high open-circuit voltage and peak power densities using lower temperatures is also a problem (Dinçer & Siddiqui, 2020). On the other hand, recent studies on co-combustion of ammonia in CFB boilers indicate that the NO_x emissions are smaller at low combustion temperature. It provides a direction for further research into reducing NO_2 emissions (Kim et al., 2023b). For the marine sector, Samsung Heavy Industries (SHI) has obtained approval for its design of a 200,000 cubic-meters class, ultra-large ammonia carrier, which using an ammonia fuel system. The vessel is designed to transport significant amounts of ammonia without producing any CO_2 emissions during operation (Njovu, 2023).

The applications of ammonia are still challengeable. However, existing and ongoing research related to ammonia indicates the feasibility of using it as a fuel. Moreover, with the advancements in technology, there is optimism for the future of ammonia fuels as a sustainable and efficient energy solution.

5 Conclusions

Renewable energy plays an important role in the context of global environmental issues and the energy crisis. Ammonia, a clean and alternative fuel, is considered to be the most potential fuel due to its high energy density, convenient storage and availability of production infrastructure. Ammonia has a promising development future and the topic of using it as a fuel has regained interest recently.

In recent years, ammonia fuel has been studied in different fields such as gas turbines, internal combustion engines, fuel cells and the marine industry. Ammonia is considered to be a suitable alternative fuel for vehicles and marine engines in terms of safety and environmental protection. However, the issue of NO_x emissions during combustion, which are caused by incomplete combustion or environmental factors, remains a challenge. It limits the further advancement of ammonia fuels.

Ammonia-fueled gas turbines have less effective data related to their performance and efficiency compared to conventional gas turbines. Through extensive studies, issues like flame instability and the combustion efficiency of ammonia fuel are being brought to the public's attention. A number of researchers have focused on conducting different studies to improve the performance of ammonia in gas turbines. This includes using a cyclone for flame combustion stabilization and a flame stabilizer to improve combustion efficiency.

The use of pure ammonia as a fuel in internal combustion engines is restricted due to its poor combustion characteristics. Ammonia fuel's potential as the sole fuel in internal combustion engines is restricted due to its high auto-ignition temperature, high ignition energy demand, and sluggish combustion speed. Researchers have conducted numerous studies on blending ammonia with other fuels to better use it as a fuel for internal combustion engines. Compression ignition engines can obtain similar or greater performance compared to diesel engines by blending with fuels that have low self-ignition temperatures, such as diesel, biodiesel, and ethanol. For SI engines, larger compression ratios can be used to produce higher efficiency compared to gasoline engines. Engines using ammonia-methane blended fuel had poor performance, while those using ammonia-hydrogen blended fuel were desirable.

Ammonia fuel cells are also playing an important role. Recent studies have developed many different catalysts to enhance the output voltage of direct ammonia fuel cells. In addition, the stability and conductivity of ammonia fuel cells have also been improved by the combination of electrolytes with various ions. Further exploration of ammonia fuel cells for marine industries should be promoted due to its excellent energy efficiency and emissions performance. Ammonia-coal combustion in boilers in Japan has carried out the feasibility of tests, the de-

velopment of related applications is promising. However, there is still a need to promote more tests related to the ammonia-coal combustion boiler. In order to further explore the combustion process involved in ammonia and coal blending, ammonia combustion characteristics of different coal-fired facilities in the test also need to focus on research. Meanwhile, the advantages of ammonia as a marine fuel have been widely recognized, leading more and more manufacturers to invest in research on ammonia-fueled ships. It is expected that nearly half of all ships will be fueled by ammonia during the next ten years. However, ensuring the safety of ammonia in both human and marine environments is an important issue because of its toxicity and corrosiveness.

Using ammonia as a fuel is still challenging. The obstacles are mainly related to its activity, NO_x emissions and safety issues. Future research should focus on improving the stability of combustion, decreasing NO_x emissions, and optimizing storage and transportation. Despite the challenges, existing research and development directions for ammonia show its feasibility as a fuel. The increasing attention and study of it worldwide indicates its advancement and potential uses in different sectors. It is worthwhile for ammonia to be continued and expanded in research activities as a fuel in different fields.

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