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A Review on Combustion Technologies for Ammonia-Diesel Compression Ignition Engines: Ways to Achieve High Ammonia Substitution

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Abstract Ammonia, as a zero-carbon fuel, has great potential to meet decarbonisation targets in the internal combustion engine sector. This paper summarises recent studies in which ammonia is used as a fuel for compression-ignition engines. As ammonia has low combustion reactivity, it therefore needs to be used in conjunction with high reactivity fuel, such as diesel, to ensure stable engine operation. At present, there are two routes to supply ammonia to the engine combustion chamber, namely ammonia port injection route and ammonia in-cylinder direct injection route. In the two technical routes, the ammonia-diesel engines are usually exposed to the problems of low ammonia energy rate (AER), limited thermal efficiency, and high emissions of nitrogen-containing pollutants, especially at the high ammonia substitution conditions. Aiming to the solutions to these problems, this study summarises the engine combustion technologies with relatively high AER, such as premixed charge compression ignition (PCCI) and reaction-controlled compression ignition (RCCI), and analyses the effects of the advanced combustion technologies on the combustion and emissions characteristics of the ammonia fuelled engine. This paper further summarizes the engine combustion technologies at ultra-high AER, and finds that the use of diesel pilot technology and ammonia-diesel stratified injection is expected to achieve stable engine operation. This review provides researchers with insights, challenges, and perspectives on the ammonia-diesel engine combustion technologies.

Keywords Dual-fuel engine; Ammonia energy rate; Compression ignition; Combustion technology; Emissions control

1. Introduction

Global warming and energy shortage requires a transition of the world's energy structure towards low-carbon, efficient, and clean solutions [1]. Over the past three years, carbon emissions from the transportation sector accounted for 18.9%, 19.6%, and 20.1% of the total global carbon emissions [2]. Carbon dioxide is the most impactful greenhouse gas contributing to global temperature rise, causing approximately 30% of climate warming [3]. According to the Paris Agreement (COP21), carbon emissions reduction in the transportation sector is a crucial step in the global effort to achieve carbon

reduction targets [4-10]. In the transportation sector, internal combustion engines play a crucial role in long-distance heavy-duty trucks, ships, and other areas [11]. The application of zero-carbon and carbon-neutral fuels in internal combustion engines, alongside the development of energy-saving and emission-reduction technologies, holds transformative strategic significance to achieve carbon neutrality in both the transportation and energy sectors [12-15].

Ammonia, a fuel for powertrain systems, possesses several advantageous properties, including hydrogen content of 17.7% [16,17], energy density of 18.6 MJ/Kg [18], low production cost [19] and mature production technology. Despite its relatively low energy density, ammonia has a significantly lower stoichiometric air/fuel ratio than typical hydrocarbon fuels, and more ammonia can be burned with the same amount of air. As a result, ammonia-air mixtures have a higher energy content per unit mass of the stoichiometric mixture. As a zero-carbon fuel, ammonia can make a unique contribution to the future energy transition by highly replacing conventional fuels. Figure 1 provides a summary of the production, storage, transportation and application of ammonia. Currently, ammonia can be produced by the Haber-Bosch method, solid-state ammonia synthesis technology, and photocatalytic ammonia production, which results in zero carbon emissions throughout the production and consumption cycle [21, 22]. Ammonia can be completely liquefied at 298.15 K and 0.9 MPa, and is predominantly stored and transported in liquid state. Ammonia can be utilised in a multitude of applications, including in ships, heavy trucks, power generation, and fuel cells. Consequently, ammonia fuel has the potential to serve as a viable solution for the green transition of future energy systems [23].



Fig. 1 The summary of the production, storage, transportation and application of ammonia

In heavy-duty engines, the majority utilize diesel as the fuel for compression ignition engines. Using zero-carbon fuels based on the existing structure of diesel engines can help reduce the costs associated with energy system transformation [24,25]. Due to ammonia's good anti-knock properties [26,27], it is possible to improve engine thermal efficiency by employing higher compression ratios [28]. Compression ignition engines offer better torque characteristics and a wider power range, making them more versatile compared to spark ignition engines. Therefore, ammonia fuelled engines, in which ammonia is ignited using highly reactive fuels, hold significant application potential [29], and dual-fuel compression ignition engines using diesel to ignite ammonia become a focal point of research. Table 1 summarizes representative studies of ammonia-diesel engines with high ammonia substitution rates, including engine structural parameters, test conditions and brief conclusions. Details of the related researches will be introduced later. Solutions are available to achieve stable combustion in ammonia-diesel engines, however, researches on combustion technologies for ammonia-diesel engines with ultra-high AER are relatively limited. As increased ammonia energy ratio leads to reduced carbon emissions, how to increase the ammonia energy ratio (AER) remains a key issue for ammonia-diesel engines.

This paper reviews the technical routes of ammonia-diesel dual-fuel compression-ignition engines, especially the combustion technologies for ammonia-diesel engine at high AER. The development targets of ammonia-diesel engines include high AER, high thermal efficiency, and low emissions. To achieve such goals, adjustment of both the mixture reactivity and the mixture spatial distribution is needed. The combustion modulation strategies that could be used to achieve the targets of ammonia-diesel compression ignition engines are summarised in Fig. 2. Mixture reactivity adjustment methods include reaction-controlled compression ignition (RCCI), premixed charge compression ignition (PCCI), turbulent jet combustion chamber, diesel pilot injection, intake air temperature control, which mainly improve combustion efficiency by controlling the reaction of the mixture. The ways to modulate mixture space distribution include adjustment in the in-cylinder injection timing, variable compression ratio, variable valve timing, exhaust gas recirculation, ammonia-diesel stratified injection mode, which improve the engine performance by optimizing the fuel and air mixing.

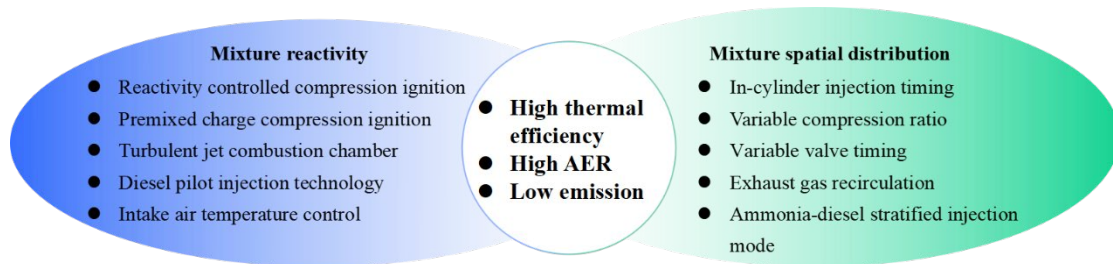


Fig. 2 Technologies for ammonia-diesel compression ignition engines

Table 1 Summary of ammonia-diesel engine combustion technology

Fuel	Engine parameter	Operating condition	Method	Features and Outcome	Researchers
Ammonia PFI Diesel DI	Single-cylinder CI engine Bore×Stroke: 137.2 × 165.1mm Displacement volume:2.44L	CR:16.25 Speed:910 rpm BMEP:0.81 MPa	Experment and simulation	AER:0-40% Start of combustion (SOC) :-4.8 to -3.2°C ATDC Peak cylinder pressure:85.4 to 80.8bar ITE:38.1% to 37.2% NO emission: 5.39 to 2.22 g/kW.h	Yousefi et al.[58]
Ammonia PFI Biodiesel DI	Multi-cylinder CI engine Bore×Stroke: 106×127mm Displacement volume:4.5L	CR:17.0 Speed:1000-1800 rpm Engine torque:280 ft-lb	Experment	AER:40%-80% Fuel conversion efficiency:38.5 to 28.2% NO _x emission:850 to 400ppm Max AER:95%	Reiter et al.[60]
Ammonia PFI Diesel DI	Single-cylinder CI engine Bore×Stroke: 137.2 × 165.1mm Displacement volume:2.44L	CR:16.25 Speed:910 rpm BMEP:0.81MPa	Experment and simulation	AER:40% Split diesel injection strategy versus single diesel injection strategy ITE:39.72% versus 38.36% Greenhouse gas (GHG): 478.10 g/kW.h versus 606.20 g/kW.h	Yousefi et al.[59]
Ammonia DI Diesel DI	Two-stroke single-cylinder CI engine Bore×Stroke: 150 × 225mm Displacement volume:3.97L	CR:13.8 Speed:375 rpm	Experment	AER:50% Liquid ammonia in-cylinder direct injection Jet-controlled compression ignition (JCCI) Diesel injection timeing:-12 to -6°C ATDC Liquid ammonia injection timing:-16 to 0°C ATDC	Zhang et al.[67]
Ammonia DI Diesel DI	Single-cylinder CI engine Bore×Stroke: 80 × 69mm Displacement volume:0.3468L	CR:17.5 Speed:1500 rpm	Experment	AER:40%-60% Liquid ammonia in-cylinder direct injection Diesel injection timing:-15°C ATDC Ammonia injection timing:-80 to 2.5°C ATDC Max ignition daley time:-25°C ATDC, 0.85–0.89 ms	Bjørgen et al.[71]
Ammonia PFI Diesel DI	Multi-cylinder CI engine Bore×Stroke: 114 × 130mm Displacement volume:1.327L	CR:18 Speed: 900-1800 rpm	Experment	AER:55%-88% Diesel injection timing:-10 to -70°C ATDC At 900 to 1200 rpm, AER achieved 88 % Max ITE:47%, at 1800rpm, AER 55%, diesel injection timing -40°C ATDC	Mi et al.[79]

Table 1 (cont.)

Fuel	Engine parameter	Operating condition	Method	Features and Outcome	Researchers
Ammonia PFI Diesel DI	Multi-cylinder CI engine Bore×Stroke: 116 × 150mm Displacement volume:1.56L	CR:18.5 Speed:900-1300 rpm IMEP:0.2-1.8MPa	Experment	AER:20-60% Particle emission: accumulation-mode particles to nucleation-mode particles Premixed charge compression ignition mode versus diesel pilot mode IMEP = 0.6 Mpa,ITE of PCCI mode > diesel pilot mode IMEP > 0.6 Mpa,ITE of diesel pilot mode > PCCI mode AER:40%-70%	Pei et al.[81]
Ammonia PFI Diesel DI	Single-cylinder CI engine Bore×Stroke: 116 × 150mm Displacement volume:1.56L	CR:18.5 Speed:1000 rpm IMEP:0.6 MPa	Experment and simulation	Premixed charge compression ignition mode At 50% AER and -40°C ATDC diesel injection timing, GHG emission: 235.07 g/kWh At 100MPa diesel injection pressure, GHG emission: 205.55 g/kWh	Wu et al.[82]
Ammonia PFI Diesel DI	Optical rapid compression machine Diesel injector nozzle diameter: 0.12mm,0.18mm,0.28mm Diesel injection pressure:80Mpa, 120Mpa	-	Experment	AER:0-95% At 95%AER,ignition daley time:35ms At 66%AER,ignition daley time:78ms AER>80%, NH ₃ premixed combustion dominant the flame propagation	Zheng et al.[92]
Ammonia PFI n-Dodecane DI	Single-cylinder CI engine Bore×Stroke: 85 × 88mm Displacement volume:0.5L	CR:16.4 Speed:1000 rpm	Experment	Max AER:98.5% Splitting n-dodecane pilot injection strategy Reaction-controlled compression ignition mode Early split: pre-injection:-80°C ATDC main injection: near TDC Late split: both injections set near TDC with a gap of 4 or 5°C between them	Rousselle et al.[99]
Ammonia PFI Diesel DI	Multi-cylinder CI engine Bore×Stroke: 130 × 161mm Displacement volume:12.8L	CR:15.2 Speed:1500 rpm IMEP:1.78-2.34MPa	Experment	AER:30%-90% Engine thermal efficiency: 48.3% to 38.9% Diesel pilot two-stage injection strategy Max AER:95% Engine thermal efficiency: 40.2%	Qiu et al.[100]
Ammonia DI Diesel DI	Two stroke multi-cylinder CI engine Bore×Stroke: 520 × 2658mm Displacement volume:0.5L	CR:21.8 Speed:103.2 rpm BMEP:2.3MPa	Simulation	AER:75%-99% Ammonia and diesel fuel share one injector Ammonia-diesel stratified injection mode Single stratified injection versus multiple stratified injection	Liu et al.[105]

2. Ammonia fuel properties

The physicochemical properties of a fuel play an important role in affecting its combustion characteristics. A comparative analysis of the physicochemical properties of ammonia with other conventional fuels, as presented in Table 2, highlights the distinctive features of ammonia. Understanding the fundamental combustion characteristics of ammonia is essential for designing ammonia-based combustion systems. Researches have investigated these characteristics [30,31], revealing several inherent limitations of ammonia as a fuel, including its high auto-ignition temperature [32], low laminar flame speed [33-35], and reduced combustion stability [36-38]. These unfavorable properties result in suboptimal combustion performance and impose significant constraints on the practical application of ammonia as a primary fuel. For instance, utilizing pure ammonia in compression-ignition engines necessitates compression ratios over 35 to achieve ignition [39]. Such elevated compression ratios substantially increase the mechanical and thermal stresses during engine operation, heightening the probability of engine failure [40]. Consequently, employing highly reactive fuels as ignition agents has become a requisite to enable the use of ammonia in compression-ignition engines [41].

Table 2 Physical and chemical properties of ammonia and other fuels [16-18,60]

	Ammonia	Hydrogen	DME	Gasoline	Diesel
Chemical formula	NH ₃	H ₂	CH ₃ OCH ₃	-	-
Density /(g· cm ⁻³)	0.68	0.07	0.67	0.75	0.86
Boiling point /°C	-33	-253	-25	33-190	>200
Latent heat of vaporization /(KJ· kg ⁻¹)	1370	445.6	467	306	270
Stoichiometric air-fuel ratio	6.06	34.3	9.0	14.6	14.5
Lower heating value /(MJ· kg ⁻¹)	18.6	120.0	27.6	44.0	42.5
Stoichiometric ratio (air/fuel)	6.0466	34	27.1	15.291	14.322
Energy content (MJ/kg-stoichiometric mixture)	2.64	4.05	1.31	2.58	2.77
Auto-ignition temperature /°C	651	585	235	248-412	226-233
Maximum flame speed /(m· s ⁻¹)	0.07	2.9	-	0.37-0.43	-
Minimum ignition energy /mJ	8	0.02	0.2	0.2-0.3	-
Flammability limit /vol%	16-25	4-75	3-18.6	1.4-7.6	0.6-5.5
Octane number	130	>100	60.6	92-98	25

To facilitate the deployment of ammonia as a viable engine fuel, it is imperative to investigate the fundamental kinetic mechanisms governing its combustion [42]. Current understanding of ammonia combustion mechanisms primarily relies on the detailed reaction pathways proposed by Miller et al. [43]. Among the feasible strategies for ammonia utilization, diesel-assisted ignition has gained attention, leading to the development of dual-fuel combustion mechanisms. However, earlier combustion models often overlooked C-N interactions, limiting their ability to accurately simulate ammonia-diesel combustion processes [44]. To address this limitation, Zhang et al. [45,46] incorporated C-N interaction pathways into their models, thereby enhancing the predictive accuracy of ignition delay times, particularly at fuel-lean conditions. Table 3 shows the reaction classes that are relevant to the NH₃/diesel

interaction [45]. Building on this work, Sun et al. [47] further refined the rate constants for C-N interactions, enabling more reliable predictions of ignition delay times and laminar flame speeds across a broad pressure range. Lai et al. [48] subsequently simplified the ammonia-diesel reaction mechanism, effectively modelling the phenomenon of high-temperature flame propagation. Fig. 3 depict the chemiluminescence images of AER60 and AER80, alongside the corresponding predicted temperature distributions in the cylinder at similar crank angle. In the visualized chemiluminescence image, a fuel-rich zone is formed in the diesel injection region, and fuel combustion produces a high-temperature yellow-white flame. The simulated high-temperature zone coincides with the distribution of the high-temperature flame, which can predict the in-cylinder combustion and temperature changes of the RCCI engine model.

The combustion of ammonia generates nitrogen-contained pollutants, including nitrogen oxides (NO_x) such as NO, NO_2 , and N_2O , as well as unburned ammonia [49,50]. The formation of thermal NO_x can be explained through the Zeldovich mechanism [51-53], while HNO and NNH intermediates play crucial roles in the production of fuel-derived NO_x [54]. In ammonia-diesel engines, ammonia burning relies mainly on diesel fuel ignition, but complete combustion of ammonia cannot be achieved in areas where diesel fuel is thinly distributed [55]. As N_2O emission mainly comes from the low-temperature oxidation and incomplete combustion of ammonia, high N_2O emissions are often associated with high unburned ammonia emissions [56].

Table 3 Reaction classes containing the NH_3 /diesel interactions [45]

No.	Reaction	A	n	E_a
Oxidation of n-hexadecane				
1	$\text{NC}_{16}\text{H}_{34} + \text{NH}_2 = \text{NC}_{16}\text{H}_{33} + \text{NH}_3$	5.33E1	3.46	5.60E+03
2	$\text{NC}_{16}\text{H}_{34} + \text{NO} = \text{NC}_{16}\text{H}_{33} + \text{HNO}$	5.00E+13	0.00	5.1E+04
3	$\text{NC}_{16}\text{H}_{34} + \text{NO}_2 = \text{NC}_{16}\text{H}_{33} + \text{HONO}$	3.000E14	0.00	3.20E+04
4	$\text{NC}_{16}\text{H}_{34} + \text{NO}_2 = \text{NC}_{16}\text{H}_{33} + \text{HNO}_2$	9.600E14	0.00	3.380E+4
5	$\text{NC}_{16}\text{H}_{33} + \text{NO}_2 = \text{NC}_{16}\text{H}_{33}\text{O} + \text{NO}$	1.36E+13	0.0	0.0
6	$\text{NC}_{16}\text{H}_{33} + \text{H}_2\text{NO} = \text{NC}_{16}\text{H}_{34} + \text{HNO}$	1.6E06	1.87	2961
7	$\text{NC}_{16}\text{H}_{33}\text{OO} + \text{NO} = \text{NC}_{16}\text{H}_{33}\text{O} + \text{NO}_2$	4.800E12	0.0	-358.0
8	$\text{NC}_{16}\text{H}_{33}\text{OO} + \text{NH}_3 = \text{NC}_{16}\text{H}_{33}\text{OOH} + \text{NH}_2$	3.00E11	0.00	22,000
9	$\text{NC}_{16}\text{H}_{33}\text{OO} + \text{NH}_2 = \text{NC}_{16}\text{H}_{33}\text{O} + \text{H}_2\text{NO}$	3.0E13	0.00	0
Oxidation of iso-cetane				
10	$\text{IC}_{16}\text{H}_{34} + \text{NH}_2 = \text{IC}_{16}\text{H}_{33} + \text{NH}_3$	5.337E1	3.46	5.60E+03
11	$\text{IC}_{16}\text{H}_{34} + \text{NO} = \text{IC}_{16}\text{H}_{33} + \text{HNO}$	5.00E+13	0.00	5.1E+04
12	$\text{IC}_{16}\text{H}_{34} + \text{NO}_2 = \text{IC}_{16}\text{H}_{33} + \text{HONO}$	3.000E14	0.00	3.20E+04
13	$\text{IC}_{16}\text{H}_{34} + \text{NO}_2 = \text{IC}_{16}\text{H}_{33} + \text{HNO}_2$	9.600E14	0.00	3.380E+4
14	$\text{IC}_{16}\text{H}_{33} + \text{NO}_2 = \text{IC}_{16}\text{H}_{33}\text{O} + \text{NO}$	1.36E+13	0.0	0.0
15	$\text{IC}_{16}\text{H}_{33} + \text{H}_2\text{NO} = \text{IC}_{16}\text{H}_{34} + \text{HNO}$	1.6E06	1.87	2961
16	$\text{IC}_{16}\text{H}_{33}\text{OO} + \text{NO} = \text{IC}_{16}\text{H}_{33}\text{O} + \text{NO}_2$	4.800E12	0.0	-358.0
17	$\text{IC}_{16}\text{H}_{33}\text{OO} + \text{NH}_3 = \text{IC}_{16}\text{H}_{33}\text{OOH} + \text{NH}_2$	3.0E11	0.00	22,000
18	$\text{IC}_{16}\text{H}_{33}\text{OO} + \text{NH}_2 = \text{IC}_{16}\text{H}_{33}\text{O} + \text{H}_2\text{NO}$	3.0E13	0.00	0
Oxidation of 1-Methylnaphtgalene				
19	$\text{C}_{10}\text{H}_7\text{CH}_2 + \text{HNO}_2 = \text{C}_{10}\text{H}_7\text{CH}_3 + \text{NO}_2$	8.14E4	1.87	4838
20	$\text{C}_{10}\text{H}_7\text{CH}_2 + \text{HONO} = \text{C}_{10}\text{H}_7\text{CH}_3 + \text{NO}_2$	8.14E4	1.87	5504
21	$\text{C}_{10}\text{H}_7\text{CH}_2 + \text{HNO} = \text{C}_{10}\text{H}_7\text{CH}_3 + \text{NO}$	1.47E10	0.76	349.0

	$C_{10}H_6CH_3+HNO=C_{10}H_7CH_3+NO$	3.78E5	2.28	456
22	$C_{10}H_7CH_2+NO_2=C_{10}H_7CH_2O+NO$	1.36E12	0.0	0.0
23	$C_{10}H_7CH_2OO+NO_2=NO_2+C_{10}H_7CH_2O$	4.70E12	0.0	358
24	$C_{10}H_7CH_2O+NO=C_{10}H_7CHO+HNO$	7.6E13	0.76	0.0
25	$C_{10}H_7CH_2O+NO_2=C_{10}H_7CHO+HONO$	4.0E12	0.0	2285

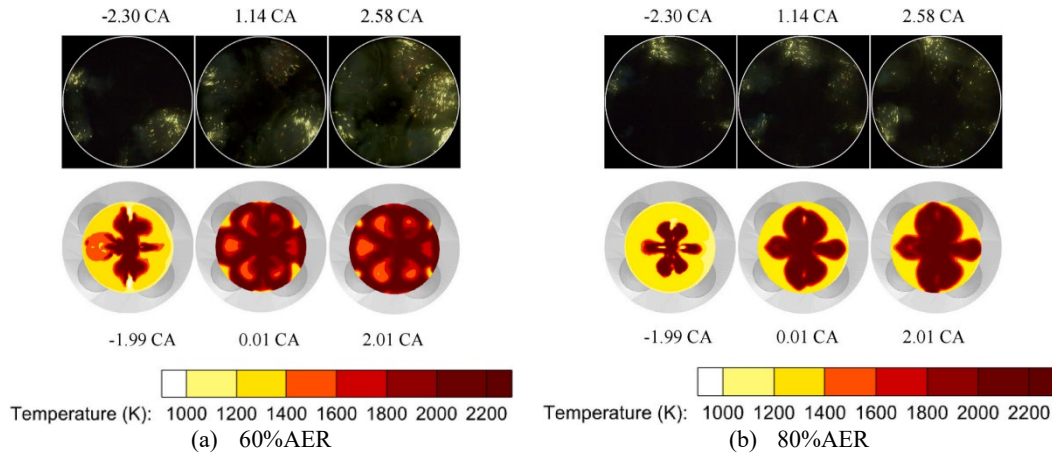


Fig. 3 Flame position in ammonia-diesel engine combustion [48]

3 Technologies for ammonia compression-ignition engines

The methods of ammonia supply to compression-ignition engines include ammonia port injection and ammonia direct injection. Fig. 4 shows a schematic diagram of an ammonia port injection configuration and a dual fuel direct injection configuration. The distinction between the two methods is that in the case of ammonia port injection, ammonia and air are supplied in a premixed state into the combustion chamber, with the spatial distribution of the diesel injection determining the ignition position. In contrast, direct ammonia in-cylinder injection requires the interaction between the ammonia spray and the diesel spray, and the high latent heat of vaporization of the ammonia may result in increased difficulty in fuel compression ignition.

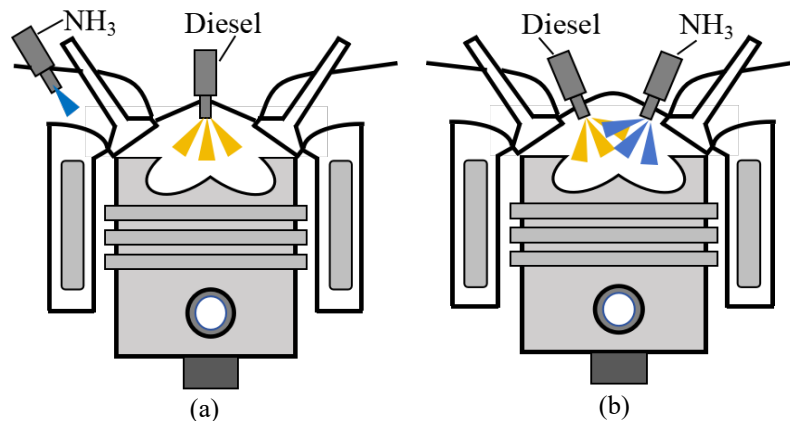


Fig. 4 Schematics of port injection configuration (a) and dual fuel direct injection configuration (b) for diesel-ammonia engines

3.1 Compression-ignition engines with ammonia port injection

Ammonia port injection delivers ammonia into the intake manifold where it mixes with air to form a mixture that enters the cylinder during the intake stroke. As the piston approaches top dead centre, diesel is injected into the cylinder, leading to fuel ignition and subsequent combustion. The combustion

process typically involves several stages, including premixed combustion of the diesel, and flame propagation of the ammonia mixture [57]. Ammonia port injection is preferred due to its simplicity in engine system modification.

However, increasing AER by ammonia port injection affects engine performance. Yousefi et al. [58, 59] investigated the combustion and emissions of an ammonia-diesel engine with AER ranging from 0% to 40%. With ammonia port injection, increasing the AER means higher concentration of ammonia in the premixed intake air, but the ammonia mixture is difficult to be ignited away from the diesel spray in the combustion chamber, resulting in a drop in engine thermal efficiency from 38.1% to 37.2%. Reiter et al. [60], through an experimental study, revealed that the fuel conversion efficiency at 95% AER was reduced by two thirds, compared to that at 60% AER.

While the use of ammonia as a fuel is effective in carbon emissions reduction, it raises the issue of NO_x and unburned ammonia emissions. Niki et al. [61] showed that the combustion process of ammonia at higher temperatures can help reduce the emission of N₂O, and the same group of researchers [62] also reported that at high torque conditions the emissions of NO_x and unburnt ammonia could be reduced. The combustion process of ammonia was more adequate, and the unburned ammonia was reduced by 11% at the high load conditions compared to the low load conditions.

3.2 Compression-ignition engine with ammonia direct injection

The application of ammonia direct injection primarily has two ways. One involves low-pressure ammonia gas injection into the cylinder in early intake stroke using a specific ammonia injector. The other method involves spraying liquid ammonia. Research on gaseous ammonia direct injection is limited, with most studies focusing on spark-ignition ammonia engines [63,64]. The direct injection system of liquid ammonia facilitates precise adjustment of the mixing ratio and ammonia combustion process optimisation, which is an important method of application in compression-ignition engines.

Direct injection of liquid ammonia could produce flashing boiling phenomenon at the nozzle outlet, which may result in non-uniform spray characteristics. It is therefore important to study the liquid ammonia spray mechanism to understand the performance of an ammonia-diesel dual fuel direct injection engine. Zhang et al. [65] investigated the liquid ammonia/air mixing characteristics at direct injection conditions, and found that the Lagrangian model can accurately reproduce the spray characteristics of liquid ammonia at non-flashing conditions, but its prediction performance is less satisfactory for the flash boiling phenomenon. To explain the spray evolution characteristics of liquid ammonia at the near-nozzle region, Zhang et al. [66] numerically studied the spray penetration behaviors of liquid ammonia injection with phase change. As shown in Figure 5(a), it is noted that the liquid ammonia penetration increased with reduced ambient pressure, whereas the penetration of ammonia vapour increased with decreased ambient density. Zhang et al. [67] further experimentally studied the characteristics of liquid ammonia spray. As shown in Figure 5(b), the lower boiling point of liquid ammonia makes its evaporation rate higher than that of diesel, resulting in shorter tip penetration distance but wider spray angle.

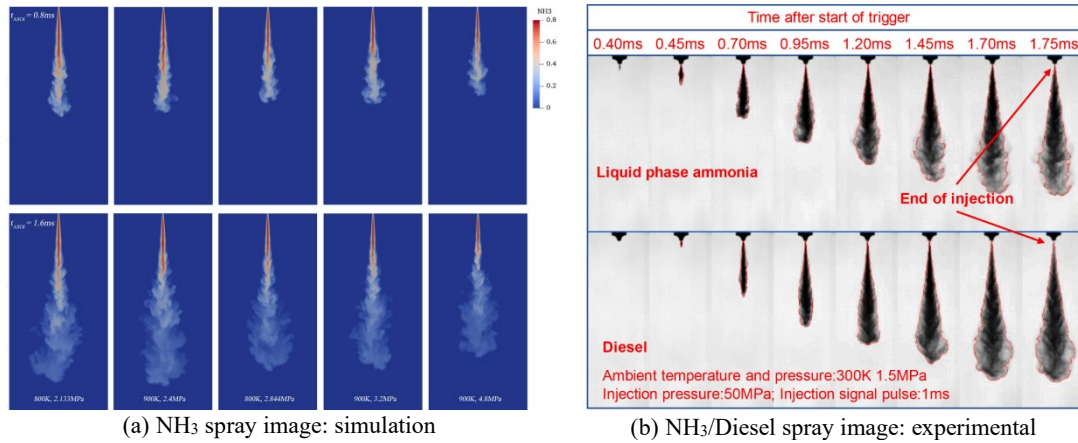


Fig. 5 Ammonia and diesel spray development [65,67].

The direct liquid ammonia injection strategy plays an important role in mixing ammonia with diesel and air in the combustion chamber. Nyongesa et al. [69] found that by installing an ammonia injector in the engine cylinder head and adjusting the injection direction, timing and pressure, AER as high as 80% could be achieved, which resulted in a reduction in CO₂ emissions by 80%. Li et al. [70] found that through high-pressure liquid ammonia injection, an indicated thermal efficiency similar to that of diesel combustion could be maintained, and unburned ammonia and NO_x emissions were reduced due to the thermal denitrification process occurring in the combustion chamber. Zhang et al. [67] used diesel jet-controlled compression ignition (JCCI) technique to ignite liquid ammonia, and it was found that the combustion phase of ammonia is very sensitive to the timing of the diesel injection. Bjørgen et al. [71] investigated the effect of liquid ammonia injection timing on engine performance by fixing the diesel injection moment at -15°CA ATDC, and found that ammonia injection from -80 to -60°CA ATDC resulted in a substantial increase in unburned ammonia emissions. Conversely, delaying the ammonia injection to -30°CA ATDC promotes premixed combustion. The optimal injection strategy was to overlap the ammonia injection timing and diesel injection timing, which resulted in combustion efficiencies up to 86%.

4 Compression-ignition engine combustion technology with high ammonia energy rate

The degradation of combustion efficiency and the increase of pollutant emissions are particularly pronounced at high AER conditions [72]. Sun et al. [73] found, through optical engine experiments, that the percentage of peak flame area (FR) and flame natural lightness (FNL) decreased by 60% and 92%, respectively, when the AER reached 80%. This indicates that high AER significantly attenuated the flame development in the combustion chamber. To achieve efficient and clean combustion at high AER, researchers have made improvements to the ammonia-diesel engine, such as optimising the combustion chamber shape, adopting advanced injection techniques and increasing the ignition fuel activity, which will be described in the following section.

The fuel spatial distribution in the combustion chamber affects the combustion and flame propagation in ammonia-diesel engines, and optimising the combustion chamber geometry and the injectors position can change the fuel spatial distribution and help improve the combustion characteristics [74]. Sehili et al. [75] used a multi-objective optimization technique to calculate the optimum piston bowl shape at the 85% AER condition. Figure 6 shows the effect of the piston geometry on the combustion process, with τ_{comb} denoting the percentage of fuel burned. Their study found that the piston cylinder boundary affects the flame propagation process, and by optimising the geometrical parameters in Fig. 6(a), they reduced the engine-out unburnt ammonia emissions by 43% and improved the thermal efficiency by 31%. Cui et al. [76] investigated the effects of injector position on

the engine performance in a liquid ammonia-diesel dual fuel direct injection engine, and showed that the position of the diesel injector with respect to the liquid ammonia determines the ammonia ignition time. When the angle between the diesel and ammonia injectors was 75°, the maximum thermal efficiency of 43.6% could be achieved at 80% AER. The engine thermal efficiency tends to decrease when the ammonia and diesel nozzles are located close to each other.

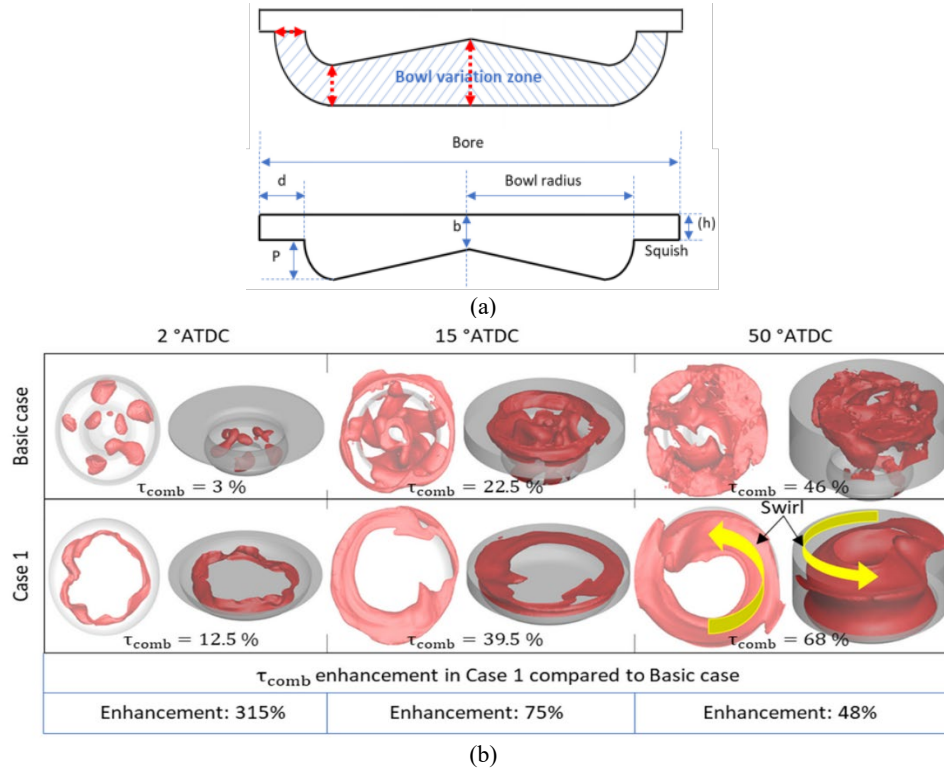


Fig. 6 Piston design parameters (a) and the effect of piston geometry on the combustion process (b).

[75].

Flexible fuel injection strategies can be used to optimize the fuel mixing and distribution in the combustion chamber by changing the injection timing, injection pressure, and injection segments [77-79]. The flexible fuel injection technologies could then result in advanced combustion strategies such as premixed charge compression ignition (PCCI) and reaction-controlled compression ignition (RCCI). In the PCCI strategy, diesel fuel is generally injected in the early compression stroke, allowing sufficient mixing time for diesel fuel with ammonia and air to form more homogeneous mixture. PCCI is especially suitable for the low or intermediate load conditions, but ignition control in PCCI is a challenge. In the RCCI strategy, diesel fuel is injected in the late compression stroke, forming an in-cylinder reactivity stratification, that is, the diesel concentrated high-reactivity region and the low-reactivity ammonia/air premixed region. Through the diesel injection control, the combustion phase and burn rate can be flexibly changed, enabling engine operation in a wide load range.

Premixed charge compression ignition (PCCI) technique mixes ammonia and air well before the compression stroke to form a homogeneous premixed gas. In the compression ignition stage, the premixed ammonia-air mixture is ignited by diesel fuel, mainly resulting in premixed combustion [80]. Pei et al. [81] found that the mixing time of diesel and ammonia could be extended by appropriately advancing the diesel injection timing in low load PCCI mode, resulting in a more homogeneous fuel mixture. It was demonstrated that an indicated thermal efficiency up to 49.5% can be obtained by injecting diesel at -40°C A TDC. Wu et al. [82] found that the key to PCCI combustion optimization of

the ammonia-diesel engine lies in tuning the reactivity and spatial distribution of the fuel blend. It is indicated that increasing the ammonia energy fraction decreases the overall reactivity of the fuel mixture, proper diesel injection timing results in more uniform fuel mixture distribution, and higher diesel injection pressure improves the fuel mixing process before ignition. The reasonable adjustment of these factors can improve the engine thermal efficiency. Zi et al. [83] further investigated the PCCI combustion mode by applying a diesel split injection strategy. Effects of injection strategy on in-cylinder OH radical distribution and heat release are illustrated in Fig. 7. Using diesel split injection significantly improved the mixture reactivity distribution at the CA10 instant, shown in Fig. 7(b), and the distribution of OH radicals was significantly expanded. Compared with diesel single-injection strategy, the start of combustion in the split injection cases occurred earlier, and the more rapid burn promoted the rise of pressure. The split diesel injection strategy could improve the spatial distribution of diesel fuel compared to single injection, resulting in more homogeneous OH radical formation. This ensured the rapid low- and high-temperature reactions and promoted complete ammonia combustion. As a result, an indicated thermal efficiency of 49.3% was achieved in the PCCI combustion mode.

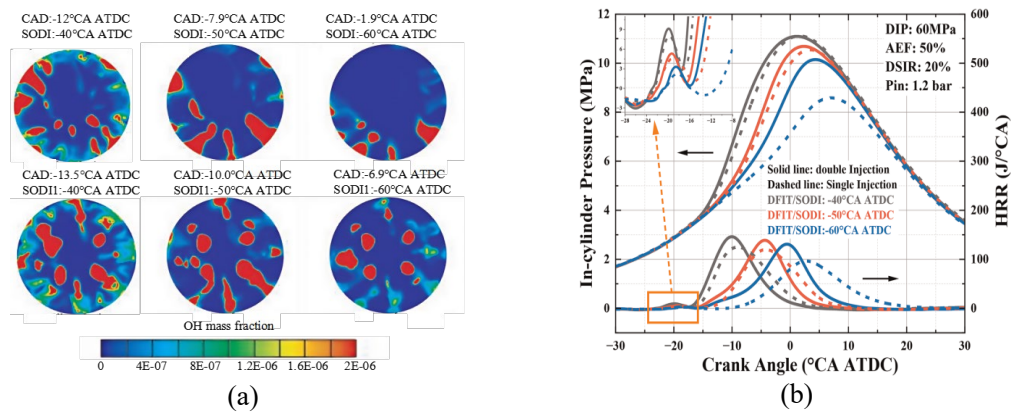


Fig. 7 Impacts of diesel injection strategy on OH radical distribution(at CA10) (a) and engine combustion characteristics (b) [82,83].

Reaction controlled compression ignition (RCCI) technology improves combustion characteristics by injecting two different reactivity fuels into the combustion chamber. The mixing ratio and injection time of the two fuels are adjusted to produce different mixing reactivity stratification. With the application of RCCI technology in ammonia-diesel engines, ammonia is injected into the cylinder early in the intake stroke to be sufficiently premixed with the air, which reduces the reactivity of the whole mixture and results in a milder combustion process. Diesel fuel is directly injected as an ignition source late in the compression stroke to ensure stable combustion [84,85]. Xu et al. [86] investigated the combustion behaviors of an ammonia-diesel dual-fuel engine, and found that ammonia-diesel RCCI combustion consists of two stages. The first stage is diffusion flame driven by diesel combustion, and the second stage is premixed combustion of ammonia/air mixture. Niki et al. [87] investigated the effect of the start time of diesel injection on engine emissions. Their results showed that early pre-injection of diesel fuel was effective in NH_3 and N_2O emissions reduction. However, it also led to an increase in NO_x , HC, and CO emissions in the ammonia-diesel RCCI engine. Fakhari et al. [88] numerically investigated the effect of intake temperature on the combustion and emissions of the ammonia-diesel RCCI engine. Fig. 8(a) shows that at the 80% AER condition, both peak cylinder pressure and peak heat release rate increase and appear earlier with increased inlet temperature. Figure 8(b) shows that higher cylinder

temperature facilitates earlier the formation of OH radicals (higher OH concentration), indicating earlier start of combustion.

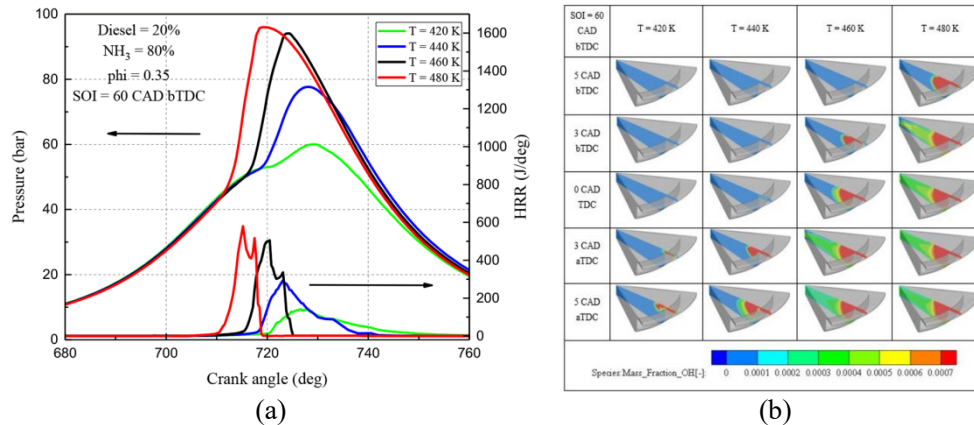


Fig. 8 The impact of intake temperature on RCCI engine performance (a) and reactive species (b) [88].

Premixing highly reactive gaseous fuels, such as hydrogen or ozone, with ammonia improves the reactivity of the mixture, reduces the need for pilot diesel, and helps achieve stable combustion at high AER. Sehili et al. [75] showed that the addition of a small amount of hydrogen improved the combustion reactivity at high loads and high AER, which improved the thermal efficiencies and ensured stable operation of the ammonia-diesel engine. Xu et al. [89] premixed ammonia and hydrogen into the combustion chamber, and found that the addition of hydrogen accelerated the ammonia combustion rate in the RCCI engine. However, when the energy share of hydrogen exceeded 30%, the ammonia-hydrogen mixture would spontaneously burn in the compression stroke before diesel injection, resulting in a 60% increase in NO emissions compared to the case without hydrogen. Lang et al. [90] investigated the effect of ozone addition on the performance of an ammonia-diesel RCCI engine at low load conditions. Fig. 9 shows the flame development images at different ozone concentrations. The addition of ozone can effectively replenish the OH radical pool during the combustion process. Flame propagation was faster, and the flame area and brightness significantly increased after ozone addition. At the test conditions, the addition of 1200 ppm ozone led to an IMEP increase by 12%, and the addition of 1600 ppm ozone resulted in a reduction in ignition delay by over 50%.

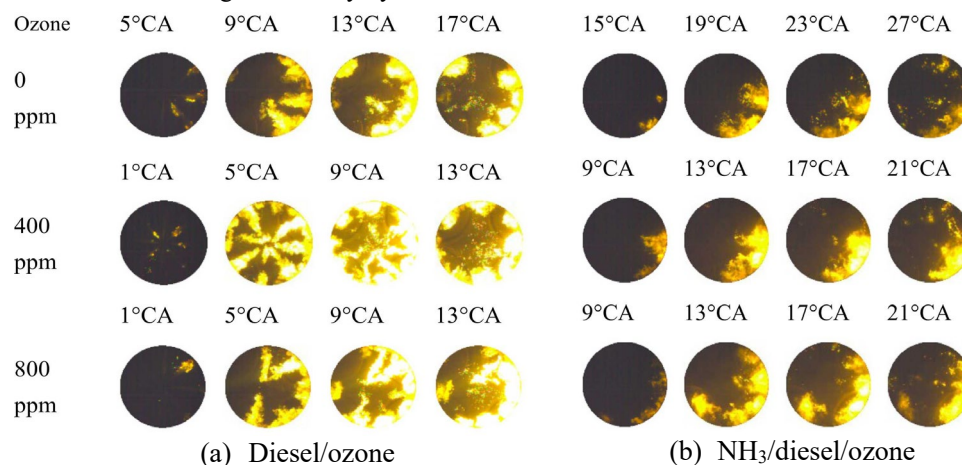


Fig.9 Flame development images at different ozone addition levels [90].

5 Compression-ignition engine combustion with ultra-high ammonia energy rate

The dependence of ammonia-diesel engines on fossil fuels can be reduced by minimising the amount of used diesel, and it is therefore necessary to explore ways to ensure stable combustion in ammonia-diesel engines at ultra-high AER. In this study, ultra-high AER is defined as a situation where the

ammonia energy fraction is over 90% of the total energy. The key to stable operation of ammonia-diesel engines at ultra-high AER is to use a very small amount of diesel fuel to ignite the ammonia [91]. Zheng et al. [92] used an optical rapid compression machine to study premixed ammonia combustion processes by diesel ignition. Fig. 10 shows the ignition and combustion process of ammonia-diesel engine at different AER. The results show that at lower diesel injection pressures or with larger diesel nozzle diameters, diesel can rapidly mix with the ammonia near the nozzle, resulting in a significantly shorter ignition delay time at 95% AER. Liu et al. [93] advanced the diesel fuel injection timing to create a high-temperature reactive environment in the combustion chamber. Through a numerical simulation, they found this reactive environment was able to support stable ignition at AER over 90%.

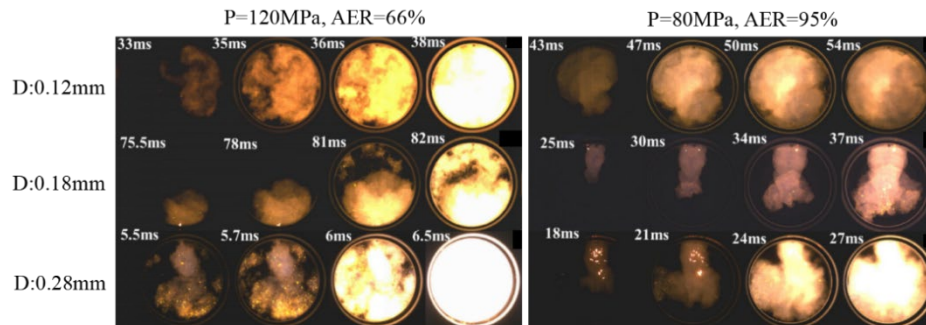
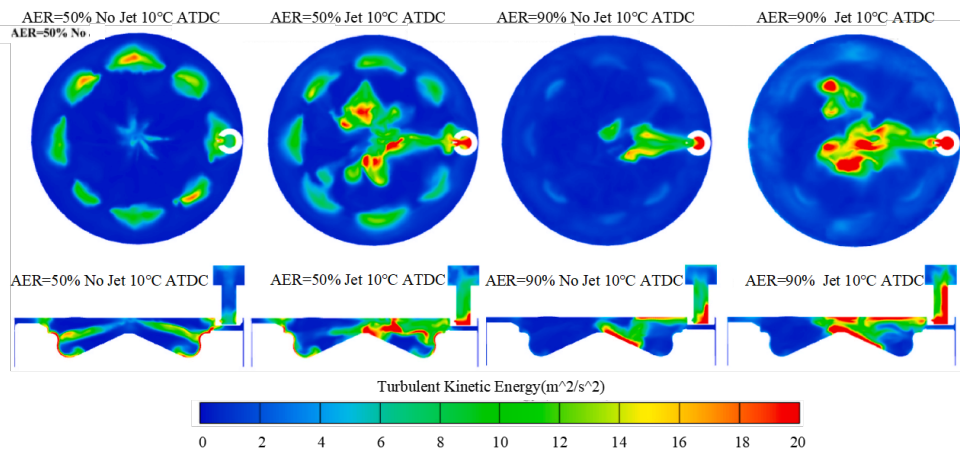


Fig.10 Ignition and combustion processes of engine at different AER [92].

Some other typical efforts to achieve ultra-high AER in ammonia-diesel engines include turbulent jet combustion chamber technology (TJCC), diesel pilot injection, and ammonia-diesel stratified injection. The turbulent jet combustion chamber (TJCC) improves the fuel mixing and ignition process by introducing turbulence effects. In this technology, diesel fuel is first injected into TJCC, and then ignited by piston compression. Combustion in the TJCC produces high-temperature and high-pressure combustion products, which rapidly enter the main combustion chamber through the turbulent jet orifice. Turbulent jet causes strong turbulent mixing in the main combustion chamber, and promotes the ignition and combustion of ammonia [94]. In a numerical study, Yang et al. [95] achieved an AER of 90% in the ammonia-diesel engine equipped with a turbulent jet combustion chamber.



(a)

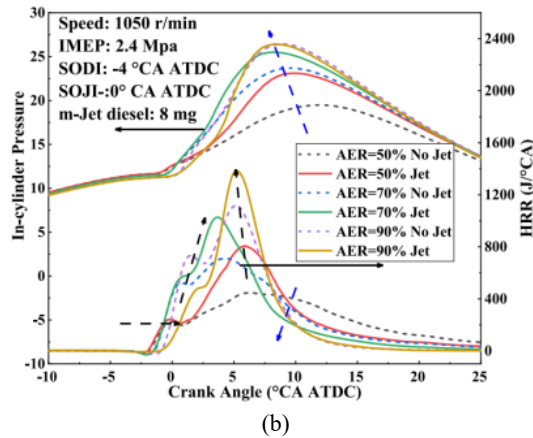


Fig. 11 Impact of turbulent jet on turbulent kinetic energy (a) and engine performance (b) at different AER [95].

Compared to TJCC technology, diesel pilot injection technology does not require a new combustion chamber structure, and it is possible to achieve stable engine combustion at ultra-high AER by adjusting the diesel injection strategy. Diesel pilot injection technology for ammonia-diesel engines uses only a small amount of diesel fuel (5-20%) injection in the late compression stroke, and the auto-ignition of diesel fuel forms a locally high-temperature flame core, triggering diffusion combustion of the ammonia/air mixture [96]. Diesel split injection technology could be used to optimise the combustion and emissions characteristics of the ammonia-diesel engines [97]. Below are some examples of the application of diesel pilot technology to ammonia-diesel engines at ultra-high AERs.

Scharl et al. [98] investigated the ignition and combustion characteristics of diesel pilot injection and liquid ammonia direct injection in a rapid compression machine. Their results showed that complete combustion could be achieved if the liquid ammonia spray was in contact with the diesel spray after diesel ignition. However, if the liquid ammonia spray had contact with the diesel spray before diesel ignition, diesel ignition was inhibited even at the full load conditions. Rousselle et al. [99] compared the effects of single and double injection strategies on the ammonia-diesel engine performance at moderate loads with diesel pilot injection technology. The results showed that both injection strategies, as diesel fuel possessed 1.5%-10% of the total energy share, could achieve complete combustion of ammonia. The double injection strategy increased the local fuel mixture fraction and reactivity, and reduced NO_x and unburned ammonia. Qiu et al. [100] conducted an optimization study on the diesel pilot injection strategy for ammonia-diesel engines. Fig.12 shows the engine combustion and emissions characteristics at changed AER and main injection timings. The maximum pressure decreases from 1.62 MPa to 1.49 MPa when the ammonia energy share increases from 30% to 90%. The first small peak belongs to the pre-injection diesel combustion, while the second peak represents the heat release from the co-combustion of ammonia and diesel. NO_x emissions show a non-monotonic changing trend, with the lowest NO_x emissions occurring at 60% AER, suggesting a transition in NO_x formation from the thermally-dominated regime to the fuel-dominated regime. By adjusting the pre-injection diesel quantity, main injection timing, and the injection interval between two injection segments, stable engine operation with an ultra-high AER of 95% was achieved, along with the engine thermal efficiency of 40.2%. It was also noted that at higher AER, increasing the engine load could improve thermal efficiency.

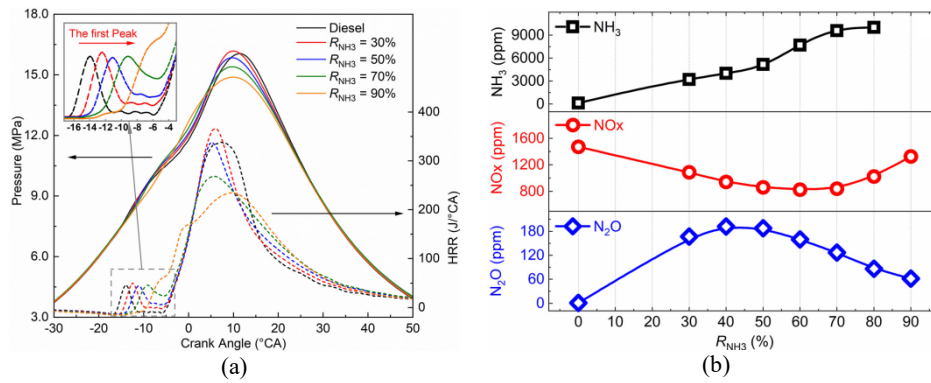


Fig.12 Engine combustion performance (a) and pollutant emissions (b) at 30%-90% ammonia substitution. [100]

Ammonia-diesel engines usually require two independent fuel injection systems for ammonia and diesel, respectively, and the in-cylinder distribution of these two fuels are influenced by their nozzle positions. An inappropriate nozzle position can affect fuel distribution, leading to a decline in engine combustion performance at high AER conditions. To address this issue, some researchers tried to use coaxial injectors to inject ammonia and diesel, and by adjusting the injection strategies for ammonia and diesel, stratified fuel distribution could be achieved [101]. Takasaki et al. [102] experimentally studied the coaxial injection technology by employing incompatible water and diesel fuel for the coaxial injection. Since ammonia and diesel fuel are also incompatible, there is also a basis to realise coaxial injection. Further, Wirbeleit et al. [103] and Bedford et al. [104] experimentally optimized the stratified fuel injection strategy using the coaxial injection technology, demonstrating that this mode can reduce NO_x and particulate emissions from diesel engines. Liu et al. [105, 106] conducted simulation studies on ammonia-diesel coaxial injection technology and stratified injection strategies in low-speed marine engines. Figure 13(a) shows the structure of the ammonia-diesel coaxial injector, while Figure 13(b) illustrates the stratified injection strategy. A single injector was used to supply ammonia and diesel fuel, and each fuel was injected by multiple times independently. Their research indicates that the initially injected diesel creates a high-temperature reaction environment, and the subsequent multiple injections of diesel promotes ammonia combustion. Coaxial injection of ammonia and diesel allows the ammonia spray reaches the diesel flame area more easily, ensuring ammonia combustion even when the relative diesel ignition energy is only 1%. These studies collectively show that appropriate injection strategies are critical for the performance enhancement for ammonia-diesel engines.

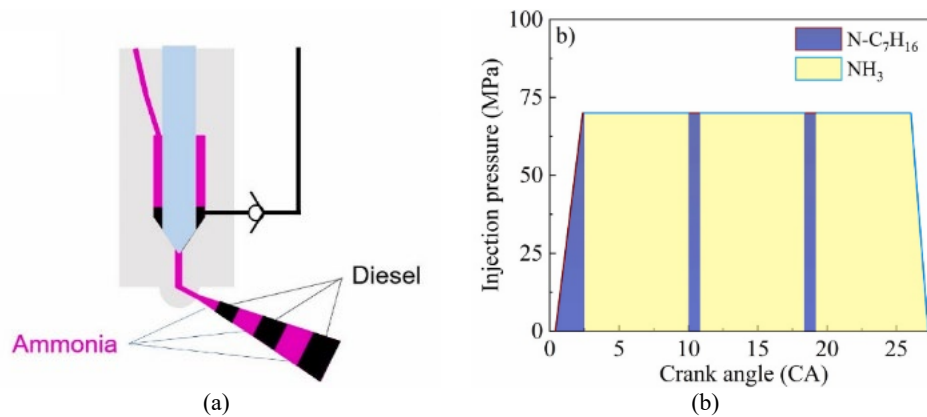


Fig. 13 Schematic of ammonia-diesel stratified injection mode (a) and injection rate shape (b) [106]

6. Summary and outlook

6.1 Summary

The application of ammonia as the fuel for combustion engines is a prospective way to achieve the decarbonisation target in the road and marine transportation industry. However, due to the ignition reluctance and slow flame propagation of ammonia fuels, fuels with high ignition reactivity, such as hydrogen or diesel-like fuels, have to be used to trigger ammonia combustion. This paper summarizes the research progress of the combustion control technologies in the past few years developed for ammonia-fuelled compression ignition engines with diesel fuel as a combustion accelerator. Fig. 14 summarises the engine strategies at different ammonia substitution rates, as well as the challenges and the solutions, focusing on the combustion technology for ammonia-diesel engines with high ammonia substitution rates.

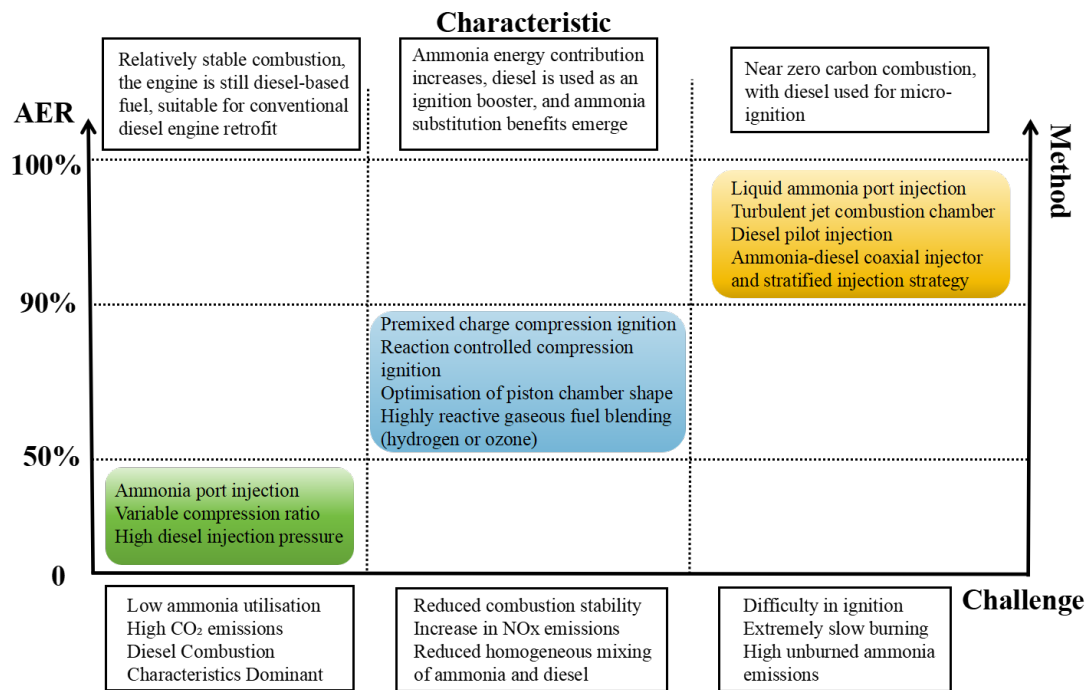


Fig. 14 Combustion behaviors, challenges, and technologies of ammonia-diesel engines with different AER

In ammonia-diesel compression ignition engines, ammonia could be either supplied to engines through intake port injection or in-cylinder direct injection. Depending on the ammonia substitution rate for diesel fuel, ammonia-diesel compression ignition engines could also be classified to ammonia-diesel dual fuel engines, in which the energy percentages of diesel and ammonia fuels are comparable, or diesel pilot ignition ammonia engines, in which the energy percentage of ammonia fuel is far higher than that of diesel fuel. Ammonia port injection technology has lower design difficulty for its less modification in the engine cylinder head. However, in early studies it was considered that high ammonia substitution rate is difficult to achieve through the ammonia port injection method, and as such researches were focused on the ammonia-diesel dual fuel combustion strategy, with the studied ammonia substitution rate usually below 80%. In contrast, liquid ammonia direct injection allows for more flexibility in the spatial distribution adjustment of diesel-ammonia-air mixture in the combustion chamber, and therefore many researches on liquid ammonia direct injection engines were focused on the diesel-ammonia spray interactions effects on engine combustion and emissions. One of the most significant advantages of liquid ammonia direct injection technology is its capability to achieve higher ammonia substitution rate and

engine thermal efficiency, but the engine cylinder head redesign and the direct injection system durability are the practical hurdles for the application of this technology.

As higher ammonia substitution rate signifies lower CO₂ emissions, many recent researches on ammonia-diesel engines tried to study the engine combustion and emissions characteristics at high or ultra-high ammonia substitution conditions, in which ammonia combustion could be triggered by diesel pilot ignition. The key to realize higher ammonia substitution rate is to reasonably organize the in-cylinder fuel-air mixing process and the spatial reactivity distribution, which could subsequently affect the flame development. PCCI and RCCI combustion strategies that enable mixture homogeneity and mixture stratification, respectively, were studied to explore the fuel mixing effects on the engine performance at the upper limit of ammonia substitution rate. The existing studies indicated that the injection strategy of pilot diesel fuel has important impacts on the mixture ignition and combustion processes at ultra-high ammonia substitution conditions. Compared to the single-stage injection strategy, split diesel injection is reported to show more robust ignition ability. Through the optimization of the injection mass in the different injection stages, as well as the injection interval, the highest ammonia substitution rate of 95% is experimentally obtained, with the engine thermal efficiency maintained at over 40%.

6.2 Outlook

Ammonia-diesel compression-ignition combustion is an important technology pathway for ammonia fuel application in internal combustion engines. Because of its minimal needs in engine structure modification and infrastructure change, it is also considered as an economic way for carbon emissions reduction in heavy-duty road transportation and maritime transportation. However, the wide application of ammonia-diesel compression ignition engines in transportation industry still faces several problems, such as how to maximize the ammonia substitution percentage to achieve the most significant carbon emissions reduction effect, how to optimize the engine thermal efficiency at ultra-high ammonia substitution conditions, and how to simultaneously control nitrogen-contained emissions such as NO_x, N₂O and unburned NH₃. Further development of combustion and aftertreatment control technologies is needed to address the above problems.

For ammonia-diesel compression ignition engine, achieving a high ammonia substitution percentage while maintaining high thermal efficiency is a complementary challenge. Enhancing the use of ammonia as a fuel substitute must be carefully balanced with improving thermal efficiency to ensure the engine operational performance. At elevated ammonia substitution conditions, it is imperative to direct attention towards the stable ignition and rapid combustion of ammonia. The physical and chemical properties of the pilot-ignition diesel have important impacts on ammonia fuel ignition. For example, the differences in the ignition effects on ammonia burn were observed for diesel and biodiesel with different cetane numbers [60,107,108]. Therefore, future researches are needed to clarify the relation of diesel properties with ammonia ignition at changed ammonia premixed atmospheres, based on which an evaluation method for pilot fuel ignition tendency could be therefore proposed and as such diesel specially used for ammonia-diesel combustion engines could be tailored. Furthermore, by integrating the pilot-ignition fuel properties, engine combustion system design, and fuel combustion process modulation, efficient engine combustion technology at high ammonia substitution rates could be developed to address the issues of limited ammonia substitution rates and thermal efficiency in ammonia-diesel engines.

Nitrogen-contained emissions such as NO_x, N₂O and unburned NH₃ are another important issue needed to be solved for ammonia fuelled engines [109]. For the nature of fuel-borne nitrogen, elevated amounts of nitrogen-contained emissions are commonly coupled with ammonia fuel combustion. The

control of these nitrogen-contained emissions cannot be achieved only by in-cylinder combustion modulation. Efficient aftertreatment technologies as such become necessity for the emissions control of ammonia fuelled engines. Selective catalytical reduction (SCR) is an effective way to reduce NO_x emissions from ammonia fuelled engines, and NH₃ emissions in the exhaust gases could serve as the reductant for SCR system [110]. However, depending on the engine operational conditions, NO_x or NH₃ emissions may be excessive, which could not realize the simultaneous reduction of the two types of emissions. Therefore, additional NH₃ supply or ammonia slip catalyst (ASC) technology is needed at the NO_x emissions excessive or NH₃ emissions excessive scenario, respectively, necessitating the real-time aftertreatment control strategy based on ammonia injection as the reductant. Additionally, N₂O, another important nitrogen-contained emission from ammonia fuelled engines, also needs effective reduction methods as it has a greenhouse effect about 300 times as CO₂ [61,62]. N₂O is considered as a low-temperature oxidation product of ammonia combustion, but the it is also produced when ammonia is reduced in ASC. Therefore, a combination of in-cylinder and aftertreatment measures are needed for N₂O reduction.

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Competing Interests

The authors declare that they have no competing interest.

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