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Hydrogen-diesel and ammonia-diesel as fuels for future diesel engines

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The search for fossil fuels substitutes has led to the increased use of carbon-free fuels. These include ammonia and hydrogen. However, independent combustion of these fuels is quite troublesome due to their physicochemical properties or requiring significant changes in the design of the combustion engine used in heavy-duty vehicles. Such designs are used in rail vehicles and other means of heavy transport. These are usually compression-ignition engines with appropriate modifications. Therefore, the article presents solutions for co-combustion of hydrogen and ammonia fuels along with typical diesel fuel. Solutions enabling co-combustion of these fuels bring various benefits, but also present some limitations. For this reason, solutions that show potential benefits in co-combustion of ammonia and hydrogen with diesel fuel have been discussed and presented.

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1. Introduction

The search for fossil fuel substitutes has led to attempts to use zero-emission (or carbon-free) fuels in the form of hydrogen or ammonia. Using carbon-free fuels is sought as the main solution since it can lead to significant reductions in greenhouse gas (GHG) emissions [6].

Ammonia, with its high hydrogen content (17.6% by mass [13]), serves as an efficient energy carrier and at the same time can be a potential replacement for traditional fossil fuels, which can help achieve carbon neutrality in many countries. It also offers significant advantages in production, storage and transport compared to hydrogen [10]. Ammonia storage for about half a year requires a cost of \$0.54 per kg of H_{2eq} compared to \$14.95 per kg H_2 over the same period [33].

Combustion of zero-emission fuels (hydrogen, ammonia) in the engine requires significant modifications (combustion chamber, piston, engine boost system), but co-combustion with diesel is generally easier to achieve with currently existing technology.

Currently, there are not many solutions using the synergy of ammonia and hydrogen. A proposal to use both fuels simultaneously was made by Lei et al. [13] in a vehicle equipped with a fuel cell and an internal combustion engine (FCEAP – ammonia-hydrogen powertrain with fuel cell (FC) and internal combustion engine (ICE)). It was proposed that hydrogen for the fuel cell be produced on board the vehicle. The drive system was modeled for a heavy-duty vehicle (which can also be used in rail vehicle drives).

2. Properties of ammonia and hydrogen

Ammonia is a colorless gas with a very strong and distinctive odor. It is lighter than air and has an alkaline pH. It has an erosive effect on some metals. It can be safely transported as a fuel due to its low reactivity. Its liquefaction temperature is –33.34 deg C at atmospheric pressure, which indicates a great potential as an energy carrier (for hydrogen this temperature is –257.7 deg C) – Table 1.

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Table 1. Physical and chemical properties of zero-emission fuels compared to conventional fuels [3, 30, 38]

Property	Units	Ammonia	Hydrogen	Methane	Gasoline	Diesel
Density at 1 bar, 25°C	kg/m^3	0.718	0.0837	0.667	736	849
Lower heating value	MJ/kg	18.8	120	50	44.5	45
Latent heat of vaporization	kJ/kg	1370	455	511	348.7	232.4
Boiling point	°C	−33.34	−252.7	−161.5	35–200	282–338
Specific heat capacity, Cp	kJ/(kg K)	2.19	14.30	2.483	2.22	1.75
Volumetric energy density at 1 bar, 25°C	GJ/m^3	11.3	4.7	9.35	33	36.4
Octane number (RON)		130	> 100	120	90–98	8–15
Autoignition temperature	°C	657	500–577	586	230	254–285
Laminar flame speed	cm/s	7	351	38	58	86
Flammability limit (φ)		0.63–1.4	0.1–7.1	0.5–1.7	0.55–4.24	0.8–6.5
Stoichiometric air-fuel ratio by mass		6.05	34.6	17.3	15	14.5
Adiabatic flame temperature	°C	1800	2110	1950	2138	2300

Ammonia can be easily liquefied at a pressure of 9 bar at room temperature, and the volumetric energy density of liquefied ammonia is about 1.6 times greater than that of liquefied hydrogen [15] (Fig. 1).

The stoichiometric equation for the combustion of ammonia is given in the following form [11]:

$$NH_3 + 0.75(O_2 + 3.76N_2) \rightarrow 3.32N_2 + 1.5\,H_2O \quad (1)$$

However, the typical reaction kinetics favor the formation of nitric oxide [33]:

$$2NH_3 + 2.5O_2 \rightarrow 2NO + 3\,H_2O \quad (2)$$

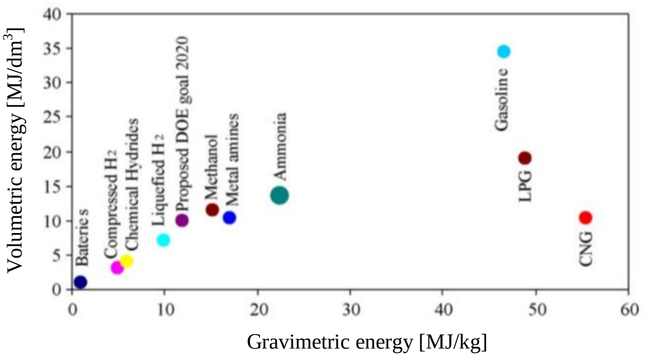

Fig. 1. Comparison of volumetric and gravimetric energy densities of various fuels [33]

The main limitation of ammonia as a fuel is the high auto-ignition temperature, low flame propagation speed and a narrow flammability range [6]. These properties limit the use of ammonia as a stand-alone fuel for internal combustion engines. Additionally, the high value of the latent heat of evaporation limits the use of ammonia as a liquid fuel, due to the increased energy required for its evaporation (this causes a temperature decrease in the cylinder).

Ammonia has a higher octane number than gasoline or methane, which makes it possible to use a higher compression ratio in the engine. In addition, combustion stability can be ensured under high load conditions [26].

The use of pure ammonia in a compression ignition engine requires a high compression ratio (around 27) and an autoignition temperature of 924 K [24]. For this reason, co-combustion of ammonia with other fuels is much more advantageous.

Figure 2 shows a schematic diagram of the possibilities of using ammonia as a fuel (or as a mixture with hydrogen). The indicated efficiency and the output energy decrease with the increase of the hydrogen content [29]. Higher engine efficiency is achieved with a leaner charge, but the highest output energy can be obtained for near-stoichiometric mixtures.

Most of the previous studies were based on the injection of gaseous ammonia into the intake manifold. Furthermore, as indicated in Fig. 2, different fuel injection strategies can be evaluated (gas phase into the combustion chamber [23], liquid injection into the intake manifold [9] or into the combustion chamber [12]). Direct injection of ammonia into the cylinder is also possible due to the various available injection strategies.

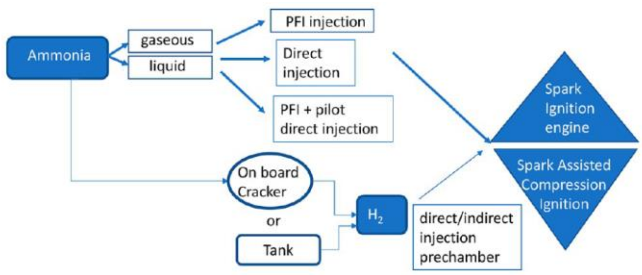

Fig. 2. Various possibilities of using ammonia as fuel in a combustion engine [29]

3. Dual-fuel diesel-hydrogen engines

The advantages of diesel co-combustion with hydrogen include [21]:

a) adding hydrogen can be used to reduce the fuel heterogeneity
b) increase of diesel flammability range by hydrogen diffusion
c) increase of flame propagation speed along with a reduction of combustion duration

d) control of ignition parameters by adding hydrogen introduced to the intake duct
e) increase in the emission of NO_x which can be controlled and reduced through the use of an exhaust aftertreatment system.

Co-combustion of diesel and hydrogen is mainly based on the fact that hydrogen is a secondary fuel in such an engine. In many studies [1, 20, 25] in which hydrogen fuel was added to diesel engines, the CO_2 emission and soot formation in exhaust emissions decreased, while an increase in the NO_x emissions was observed.

In the studies conducted by Nag et al. [20] a 7 kW engine (4-stroke, 1-cyl. $V_s = 0.661$ dm^3; $\varepsilon = 17.5$, n = = 1500 rpm) was used, in which hydrogen was injected into the intake channel along with diesel fuel at various shares of recirculated exhaust gases. The addition of hydrogen decreased the engine efficiency (BTE – brake thermal efficiency) at low and medium loads. However, a clear improvement in BTE was observed at higher loads with the addition of hydrogen. The maximum BTE was observed at 30% hydrogen energy share (HES) and 0% EGR at 100% load. Increasing the EGR share has led to a further decrease in BTE (Fig. 3).

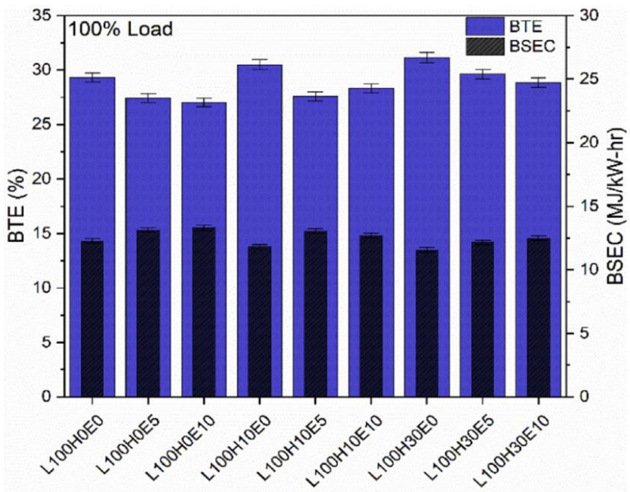

Fig. 3. Effect of HES and EGR on BSEC and BTE at 100% load [20]

The study of diesel fuel co-combustion with hydrogen and ammonia was conducted by Jamrozik and Tutak [8]. The study used a CI engine (1-cyl.; V = 573 cm^3; DI, $\varepsilon = 17{:}1$; n = 1500 rpm, $P_i = 7$ kW) with indirect, gas injection of hydrogen and ammonia.

The proportion of hydrogen and ammonia was 8%, 12%, 24% and 32%, respectively (the notation D08H2 refers to 8% hydrogen; the remaining parts are named using the same naming format).

Figure 4 shows the changing impact of adding NH_3 and H_2 to diesel fuel on the combustion duration in the cylinder of a dual-fuel engine. Hydrogen co-combusted with diesel fuel contributed to a shorter combustion duration.

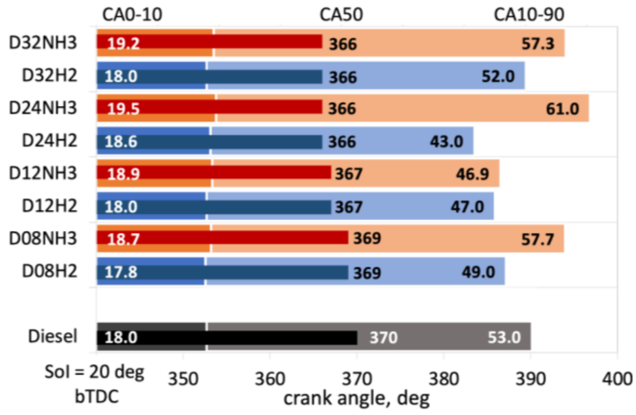

Fig. 4. Combustion phases: ignition delay (CA0–10), combustion duration (CA10–90), and the crank angle for 50% heat release (CA50), during the combustion of diesel fuel alone and ammonia/diesel and hydrogen/diesel mixtures [8]

4. Dual-fuel ammonia-diesel engines

Dual fuel systems for co-combustion of ammonia and diesel oil may include (Fig. 5):
a) low pressure injection dual fuel mode (LPDF) systems
b) high pressure injection dual fuel mode (HPDF) systems.

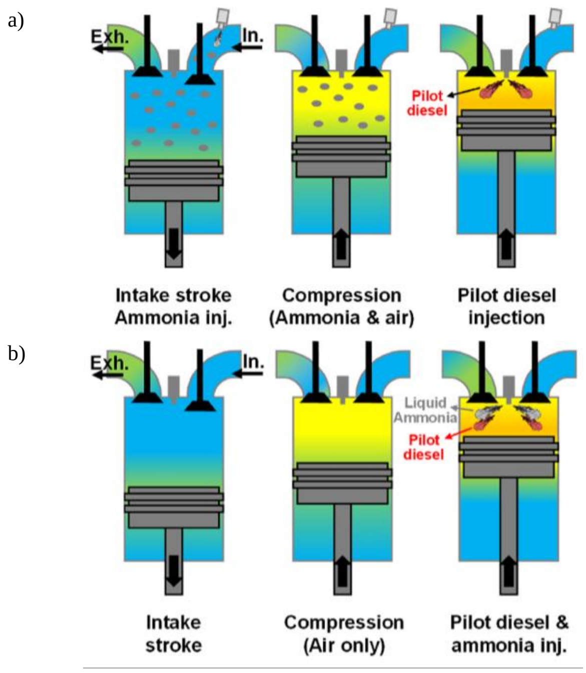

Fig. 5. The injection system concept of a) low- and b) high-pressure ammonia injection with co-combustion of diesel oil [36]

The share of ammonia during co-combustion with diesel oil is very high in terms of the energy supplied.

In the LPDF system, it is up to 90% [28], while in the HPDF system, the share of ammonia is greater at 95% [5] and can even reach 97%.

A small ignition dose of diesel oil is sufficient for co-combustion of ammonia, as it can be used to initiate the ammonia combustion process. However, increasing the share of ammonia significantly delays the onset of combustion and subsequent thermodynamic indicators (combustion center, end of combustion). The relationship between the share of ammonia and the measured combustion indicators was shown in Fig. 6.

Supplying a larger amount of gaseous ammonia to the intake manifold in order to obtain a higher AES (ammonia energy share) was found to reduce the mass flow rate of air. In addition, the calorific value of ammonia is lower compared to diesel oil, which requires a higher mass flow rate to achieve the same power as pure diesel oil. The stoichiometric air-to-fuel ratio (AFR) of a diesel-ammonia mixture decreases with increasing ammonia content, since ammonia has a stoichiometric air excess ratio of 6.0.

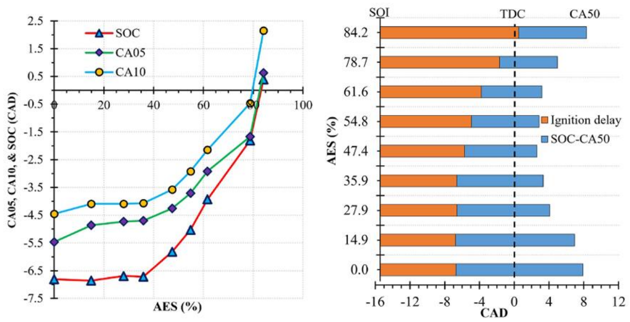

Fig. 6. Ammonia/diesel combustion characteristics indicators for different ammonia energy shares (LPDF, excess air coefficient in the range of 1.34–1.52, T_{ex} = 460–328 deg C (further points), P_i = = 3 kW) [19]

Dual fuel systems were most often designed as systems with low-pressure ammonia injection into the intake manifold. Studies of such systems were conducted by Zhou et al. [37] on a 4-cylinder turbocharged CI engine (V_{ss} = 3.26 dm^3; ε = 17.5). The studies were conducted with an increasing share of ammonia from zero to 60% at n = 1800 rpm and at partial load. A constant diesel fuel injection angle (DIT = 9 deg bTDC) was maintained at a pressure of 130 MPa.

The combustion process analysis was presented in Fig. 7. The ignition delay (defined as CA00 – start of injection to CA05 – 5% of heat released during combustion) increased rapidly above 50% of ammonia content in the combustible mixture. The high heat capacity of ammonia and its dilution effect slow down temperature-dependent reactions and extend the ignition delay period.

The combustion process duration also increases with increasing AER (ammonia energy ratio). This is because the increased ammonia content worsens the ignition characteristics of the fuel mixture by introducing strong cooling and dilution effects that together extend the combustion time.

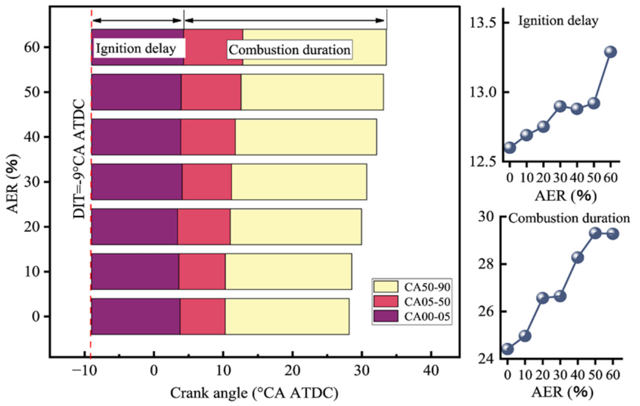

Fig. 7. Combustion characteristics indicators of dual-fuel engine at different AERs [37]

Similar studies were also conducted by Sun et al. [27], where the ammonia share was increased to 80%. The studies were performed on an engine with optical access to the combustion chamber (with indirect ammonia injection). The increased ammonia share was compensated by a smaller dose of diesel oil in order to maintain a constant fuel energy supplied to the combustion chamber. The increased ammonia share resulted in a decrease in the mean effective pressure by about 50% (at an ammonia share of 80%), and at the same time a significant delay in the so-called combustion center (CA50 – angle of 50% heat release during combustion) – Fig. 8.

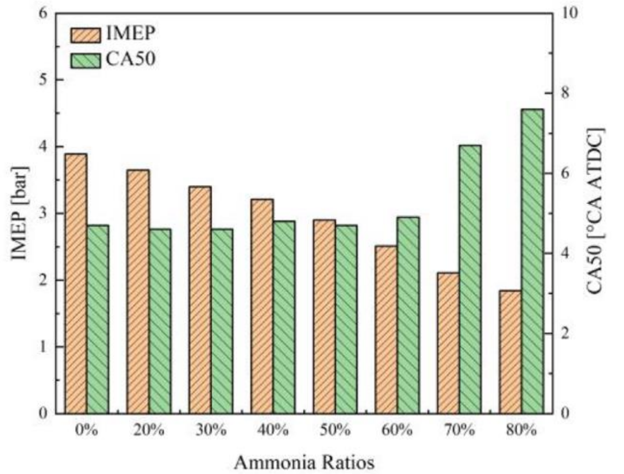

Fig. 8. Effects of ammonia ratios on the combustion characteristics of the ADDC (ammonia-diesel dual-fuel combustion) engine [27]

In large displacement engines (rail traction engines or marine engines) it is possible to use high-pressure direct injection of liquid ammonia. Co-combustion studies of the two were conducted in the form of simulations [4, 17, 36] as well as experimental studies [16, 34, 35].

Simulation studies conducted by Dong et al. [4] concerned a marine engine (S × D: 150 × 225 mm; ε = = 20:1, n = 375 rpm) with an increasing share of ammonia from 50 to 90% with high-pressure injection of both fuels (65/100 MPa ammonia/diesel). Diesel oil was injected several degrees before TDC, while ammonia several degrees after TDC in order to obtain diffusion combustion of ammonia (LADC – liquid ammonia diffusion combustion). Both fuels were injected by independent injectors located in the combustion chamber. The injection strategies have been shown in Fig. 9.

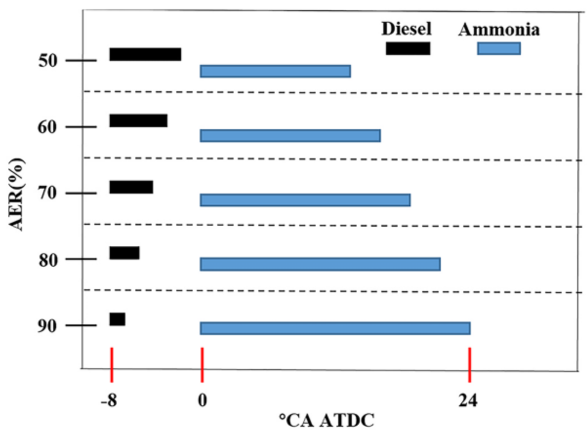

Fig. 9. Schematic diagram of liquid ammonia and diesel fuel injection time sequence [4]

The change in the trends of thermal efficiency and specific fuel consumption was shown in Fig. 10. Increasing AER initially caused an increase in ITE followed by a decrease. In relation to the combustion of pure diesel (dashed lines in Fig. 10), dual fuel combustion brings benefits when the ammonia share does not exceed 90%. Ignition of the ammonia mixture requires higher ignition energy and results in slow flame propagation and low flame temperature. All this leads to the deterioration of combustion efficiency in the dual fuel system. The conducted studies seem to indicate that the optimal ammonia share is 60%.

Studies by Zhu et al. [38] indicate that the NO_x concentration (so also NO and NO_2) initially decreased (in relation to those from pure diesel oil) and then increased when AES exceeded 40%. Similar observations were noted by Reiter and Kong conducting studies all the way back in the 1970s [2].

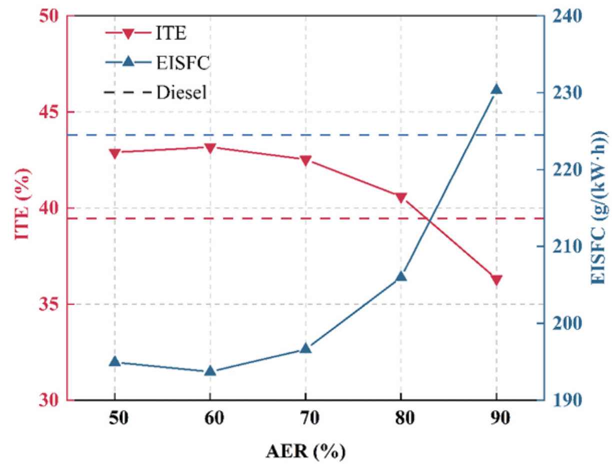

Fig. 10. Effect of AER on ITE and EISFC [4]

5. Dual-fuel ammonia-hydrogen engines

Dual fuel ammonia and hydrogen engines require an external ignition source. In this case, it is possible to supply the engine and initiate combustion with the following strategies [7, 11]:

a) high compression ratio (the increased charge temperature and flame speed result in higher engine thermal efficiency)
b) engine boost: mechanical or turbo (the increased mixture pressure and density increase the heat release rate)
c) mixtures with other fuels (ammonia with gasoline, with hydrogen, with methane, etc.)
d) ammonia dissociation (thermal reforming or cracking, formation of hydrogen and nitrogen).

The low calorific value of ammonia (approx. 18.8 kJ/kg) is of great significance in regards to the achieved engine power and its combustion efficiency. However, a mixture of 80% ammonia and 20% hydrogen has a calorific value of 21.5 MJ/kg [7].

The equation for stoichiometric combustion of ammonia with hydrogen takes the form [11]:

$$(1-\alpha_H)NH_3 + \alpha_H H_2 + \frac{3-\alpha_H}{4}(O_2 + 3.76N_2) \rightarrow \frac{3-\alpha_H}{2}H_2O + \left\{\frac{1-\alpha_H}{2} + 3.76\frac{3-\alpha_H}{4}\right\}N_2 \quad (3)$$

where α_H means the molar fraction of hydrogen.

Previous research has shown [18, 31], that the combustion properties of the NH_3/H_2/air mixture can be comparable to those of hydrocarbon fuels in engine conditions. Additionally, a high compression ratio favors the resistance of the NH_3/H_2 mixture to knock combustion. Moreover, the increase in laminar combustion velocity with the addition of H_2 (the laminar combustion velocity ratio of pure NH_3:H_2 fuels is 1:35) contributes to easier diffusion and increased reactivity and flame temperature [18].

The analysis of ammonia and hydrogen combustion was carried out with a variable hydrogen share (0–60%) but also with a variable value of the excess air coefficient (Phi (ϕ) = 1/λ = 0.6–1.2) in an SI engine [14]. One cylinder from a 4-cylinder engine (PSA) was used, and the mixture was injected in the conditions of full engine load (Fig. 11).

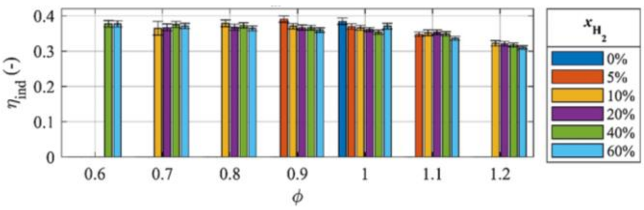

Fig. 11. Indicated efficiency analysis at full engine load (n = 1500 rpm; ε = 10.5:1) [14]

The above studies show that the addition of small amounts of hydrogen can have a positive effect for fuel mixtures supplied at close to stoichiometric. It is believed that the heat loss to the cylinder walls plays a significant role at high hydrogen content in the mixture.

Xin et al. [32] conducted an experimental study on the thermodynamics of combustion in a hydrogen/ammonia engine under partial load conditions. As shown in Fig. 12, the addition of ammonia changed the combustion characteristics by extending the combustion duration. It was defined as the angle turned between 90 and 10% of the heat released. At the same time, the fuel-air mixture combustion phase could still be controlled by modulating the ignition timing to improve the thermal efficiency (ITE) and the level of resulting NO_x emission.

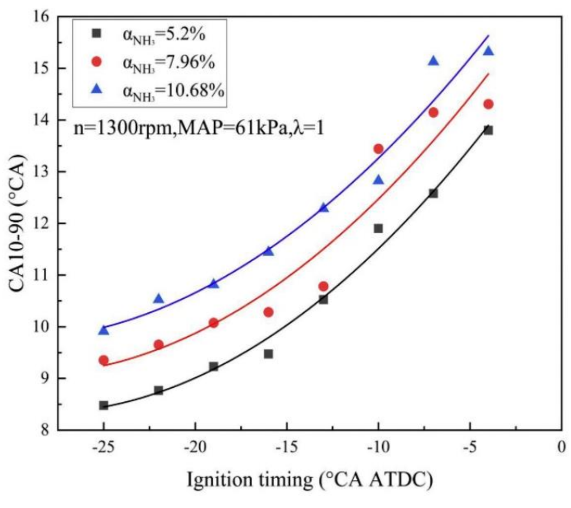

Fig. 12. Combustion durations versus ignition timing at different ammonia levels [32]

Regetti and Northrop [22] conducted research using two-stage combustion. The base fuel NH_3 was injected into the main chamber, while hydrogen was injected into the prechamber (V = 1 cm^3 and three 1.5 mm diameter nozzles). The research was conducted in the range of lean mixtures (λ = 1–2; Phi (ϕ) = 0.5–1) at different compression ratios.

The changes in combustion pressure in both chambers was shown in Fig. 13. In the case of engine fuel supply with lean mixtures, there was a clear increase in the prechamber pressure, however, a very low level of combustion pressure was achieved in the main chamber (compared to mixtures close to stoichiometric). This was caused by the low flame velocity in the main chamber, resulting from a large excess of air, which led to incomplete combustion.

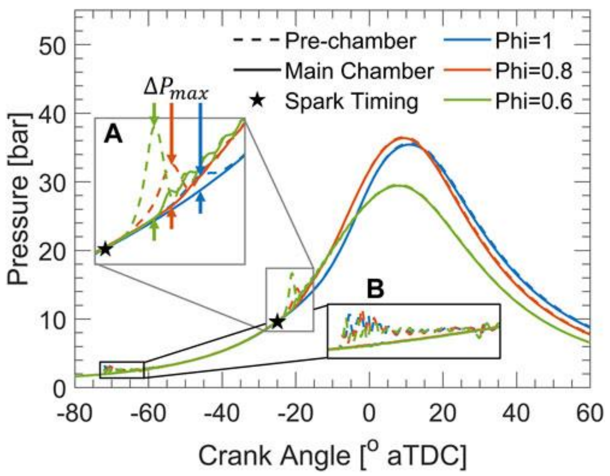

Fig. 13. Pre-chamber and cylinder pressure traces at 12:1 compression ratio at fixed spark timing (25°bTDC). Increase in prechamber pressure is highlighted during **(A)** pre-chamber burn immediately following spark timing, and **(B)** the hydrogen injection process [22]

Conclusion

The use of carbon-free fuels brings significant benefits in heavy-duty engines (including railway traction engines) when co-combusted with diesel oil; with the disadvantages of ammonia combustion in the form of: long ignition delay time, low laminar flame speed and significant NO_x emissions..

Co-combustion of diesel oil and hydrogen mainly concerns a 30% share of hydrogen. With such H_2 contents, the combustion time was the shortest, which directly means an improvement of combustion process quality.

Combustion of ammonia with diesel oil was found to be effective with an ammonia share of up to 60–80%; it was shown that it is possible to feed the engine with both low-pressure (to the intake manifold) and high-pressure (direct injection into the cylinder) systems. The addition of ammonia dilutes the mixture and lowers the temperature in the cylinder, which increases the auto-ignition delay and extends the combustion duration (with an increased share of AER).

The use of ammonia and hydrogen necessitates the use of an external ignition source. It is possible to obtain significant benefits with a high share of ammonia (up to 60%).

Two-stage combustion systems are already being designed, where ammonia is fed to the main chamber and hydrogen to the pre-chamber. Such future systems will enable lean mixtures to be burned using only carbon-free fuels.

Nomenclature

AER	ammonia energy ratio
AES	ammonia energy share
CA05	start of combustion (5% of heat release)
CA50	center of combustion
CA90	end of combustion
DIT	diesel injection time (start of injection)
EISFC	equivalent indication specific fuel consumption
GHG	greenhouse gases
HPDF	high pressure injection dual fuel mode
IMEP	indicated mean effective pressure
ITE	indicated thermal efficiency
LADC	liquid ammonia diffusion combustion
LPDF	low pressure injection dual-fuel mode
MAP	manifold pressure
n	engine speed
NO	nitrogen oxide
P_i	indicated power
Phi	equivalence ratio (Phi = 1/λ)
RON	octane number
SOC	start of combustion
TDC	top dead center
ε	compression ratio
λ	air excess ratio

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