

Ammonia Sprays for Combustion: A Review

Use of ammonia as a zero-carbon energy carrier

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Ammonia is a globally transported chemical used for a variety of applications, most notably, the production of fertiliser. Over the past decade, attention has been afforded to the use of ammonia as an energy carrier, coupling global supply of renewable energy to demand regions. Ammonia's advantages as an energy carrier include its ease of liquefaction and established international transportation routes; overcoming its low reactivity, excessive production of nitrogen oxides and its toxicity remain as challenges. For energy applications, fuel delivery is a critical aspect of effective combustion in boilers, burners and engines. Due to its adaptable phase change characteristics, ammonia fuel may be injected as a liquid or vapour, each with respective advantages or disadvantages. The focus of this review concerns the characterisation of liquid ammonia fuel injection for combustion, including recent research findings from experimental and simulation studies. Liquid ammonia injection can result in the highly dynamic so-called 'flashing' or 'flash boiling' phenomena. Research findings have been drawn from other related applications such as accidental hazardous releases. Bespoke optical experimental rigs together with diagnostic techniques and two-phase

computational fluid dynamics (CFD) simulations have enabled studies of the flashing jets under various initial or final conditions, with recent work also examining ammonia spray combustion. The review concludes with an insight into future trends and requirements for liquid ammonia combustion. Reciprocating engines for marine propulsion are cited as potential early adopters of ammonia energy.

1. Introduction

Despite technological improvements providing efficiency gains, it is anticipated that global demand for energy will continue to grow for several decades. Demand is predicted to grow by 1.8% in 2024, driven largely by a continued strong demand from Asia. Over the past 40 years there has been increasing awareness of anthropogenic emissions, particularly carbon dioxide, resulting largely from the burning of fossil fuels. Currently, oil, gas and coal continue to meet around 82% of world energy needs, despite continued growth in renewables, which (including hydro) account for 14% of primary energy usage (1). This has led to increased CO₂ concentrations in the upper atmosphere, inducing the 'global warming' effect and consequent environmental hazards. This man-made risk has been cited as one of the most complex and critical challenges facing humanity.

Wind, solar, hydro and bioenergy are the primary contributors to a global sustainable energy supply. However, wind and solar are intermittent sources which vary based on weather and seasonal conditions and provide a non-dispatchable supply. Moreover, there are vast quantities of these renewable energy resources 'stranded' in difficult-to-access or remote locations, which cannot be easily or economically recovered and transported to demand centres using direct connections to local power grids. Among the

methods for energy storage that can be used to recover these resources, chemical energy storage has been relied upon for centuries. Fossil fuels have been a testimony of society’s dependence on chemical energy storage since the industrial revolution. Natural gas is currently the predominant source of dispatchable power in the UK, but unabated, releases CO₂ into the atmosphere. To complement intermittent renewable supply, additional sources of zero-carbon dispatchable energy are required. Hydrogen from renewables is one such candidate that has been proposed and continues to be developed, while biofuels provide another option. Non-fuels based alternatives include battery storage or pumped hydro, both with their limitations.

Most recently, ammonia, a molecule that has been used widely for over a century (mainly as a fertiliser) has been presented as a potential platform for hydrogen storage and renewable power, offering ease of storage and a low cost of transportation compared to other options (2). Ammonia, which has the chemical formula NH₃, is the second most transported chemical in the world and so its international shipping market is well established. The main procedure used for ammonia production is the well-established Haber-Bosch process (3) *via* very large-scale plants capable of producing up to 3000 tonne day⁻¹, a capacity that is expected to increase substantially. Ammonia from the Haber-Bosch process can be produced utilising hydrogen from any source. Currently, the vast majority of hydrogen (approximately 79%) is derived from fossil

fuels, most commonly by steam methane reforming. Most of the remaining hydrogen production is as a byproduct of other industrial processes, with renewable sources estimated to contribute only 0.03% of total global production (4).

When zero-carbon renewable sources are used to produce hydrogen *via* electrolysis, the end product is categorised as ‘green ammonia’. Several projects seek to establish the foundations for production, distribution, storage and utilisation of green ammonia, with potential use cases including power generation and transport, as well as its continued use as a fertiliser for food production (see **Figure 1**). RWE, who considers green ammonia as one of the most competitive hydrogen vectors due to its technological maturity, has recently announced the construction of an ammonia terminal in Brunsbüttel, Germany (5).

Japan, a leading proponent for the use of ammonia, has ambitious plans for the chemical in both the process and energy industries. New Energy and Industrial Technology Development Organization has recently announced a ~US\$500 million programme dedicated to ammonia research and development. Mitsubishi Power announced the development of 100% ammonia fuelled boilers for industrial heat applications. A project to demonstrate the reliability of these systems is being conducted by JERA in their coal power stations, in parallel to their Hekinan demonstration project (6). The initiative comes in hand with the announcement of the development of the first commercial 40 MW class gas turbine design

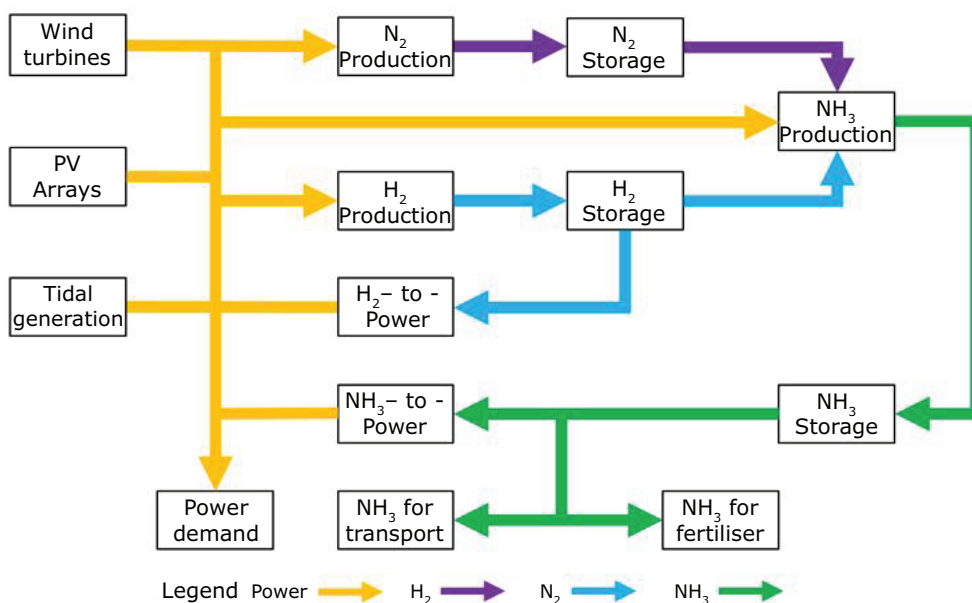


Fig. 1. Green ammonia from renewables, sector utilisation

fuelled by 100% ammonia (7). Similarly, GE Vernova and the Japan-based IHI Corporation have recently announced a collaborative agreement towards the development of a 100% ammonia capable gas turbine combustor for power generation by 2030 (8).

However, ammonia is not a drop-in fuel and issues such as high NO_x emissions and low combustion efficiencies have been identified when ammonia is deployed in combustion systems optimised for conventional fossil fuels. The reaction chemistry of ammonia-air combustion is relatively slow compared to hydrocarbon fuels, with a low heat of combustion, a slower laminar burning velocity and reduced radiation heat transfer (9). Ammonia-air flames also display poor flammability and ignition characteristics with a narrow flammability range and high ignition temperature. Another significant challenge for ammonia handling and utilisation is its toxicity which needs to be managed safely and may limit its use in certain applications.

For simplicity, much of the early fundamental combustion research and successful experimentation by combustion demonstrators has involved the use of ammonia in its vapour form. However, there are inherent limits with the vapour delivery of ammonia for large-scale or pressurised combustion systems. Early attempts to utilise liquid ammonia in gas turbines were unsuccessful owing to its high heat of vaporisation leading to significant heat loss during phase change and aforementioned poor combustion characteristics (10). With appropriate control however, modern injection systems have the potential to supply ammonia as an atomised liquid spray for transport, heat and power generation applications. There is currently limited research published in relation to liquid ammonia injection, although there has been a significant increase in interest and publications over the past three years as the potential of ammonia power has increased in credibility and popularity.

It is evident that ammonia has been gaining considerable acceptance from the industrial sector as a means for the production of power, heat and propulsion. However, greater understanding is required towards solving the operational hurdles associated with its use as a liquid fuel. The focus of this paper is to review current research relating to the use of liquid ammonia in industrial scale combustion systems, where it is inconvenient to operate with ammonia in its vapour form. Here, a review of the literature relating to the characterisation and quantification of the liquid ammonia fuel injection process is presented, evaluating both the work of modelling and experimental research programmes.

An overview of recent ammonia spray combustion studies completes the review.

2. Ammonia Spray Phenomena

When considering the use of liquid delivery and sprays for ammonia, it is important to understand the difference in how the fuel is prepared and delivered to the region in which combustion occurs. For industrial heat and large-scale power generation, burners which produce 'stationary' flames are ubiquitous. **Figure 2** shows an example of the coupling between liquid fuel spray development and combustion for a stationary flame. For these types of systems, it is the interaction between the fuel spray and the combustion air which is key in determining the overall efficiency and emissions performance.

Other applications, such as reciprocating engines, require the formation of a dispersed two-phase fuel mixture, through which the flame propagates; as shown in the numerical simulations of An *et al.* (12) in **Figure 3**.

The use of an injector (or atomiser) to introduce liquid ammonia either immediately before, or directly into, the combustion system has the capacity to simplify the fuel control system and facilitate combustion at increased pressures. Avoiding the requirement for pre-vaporisation hardware can also potentially increase overall efficiency. Much like fossil fuels, the challenge of the concept is related to the requirement to limit the emission of NO_x, nitrous oxide and unburned fuel. The technological developments that occurred in the automotive sector, first with the introduction of injection systems controlled by advanced engine control units (ECUs) and later with

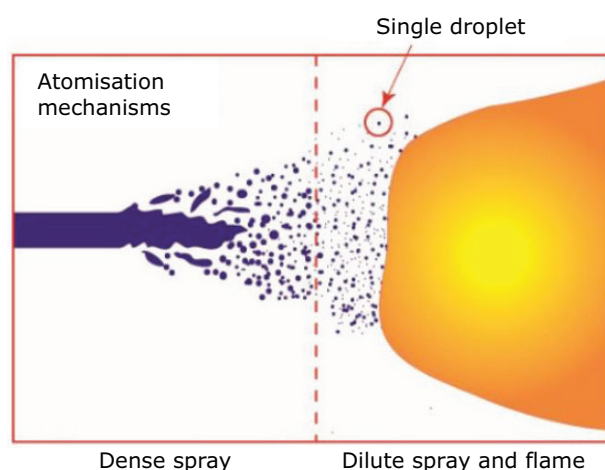


Fig. 2. Schematic representation of liquid fuel spray combustion, Reproduced from (11) Under Creative Commons Attribution Licence 4.0 (CC BY)

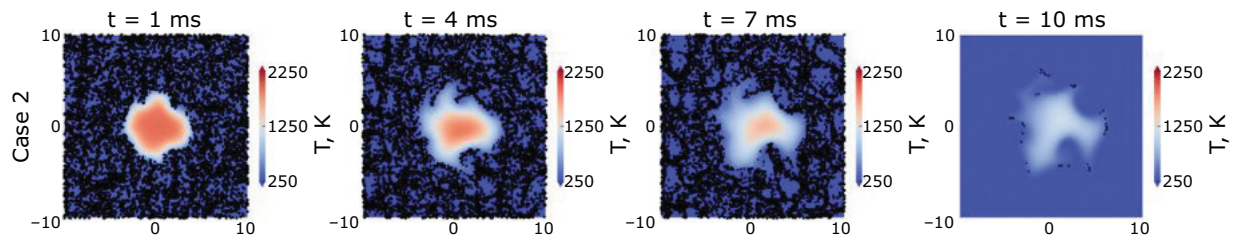


Fig. 3. Temporal evolution of gas temperature through a droplet suspension, where droplets are shown as black dots and sizes determined by their diameters (enlarged by around $\times 40$ for visual clarity) Reprinted from (12) with permission from Elsevier, 2024

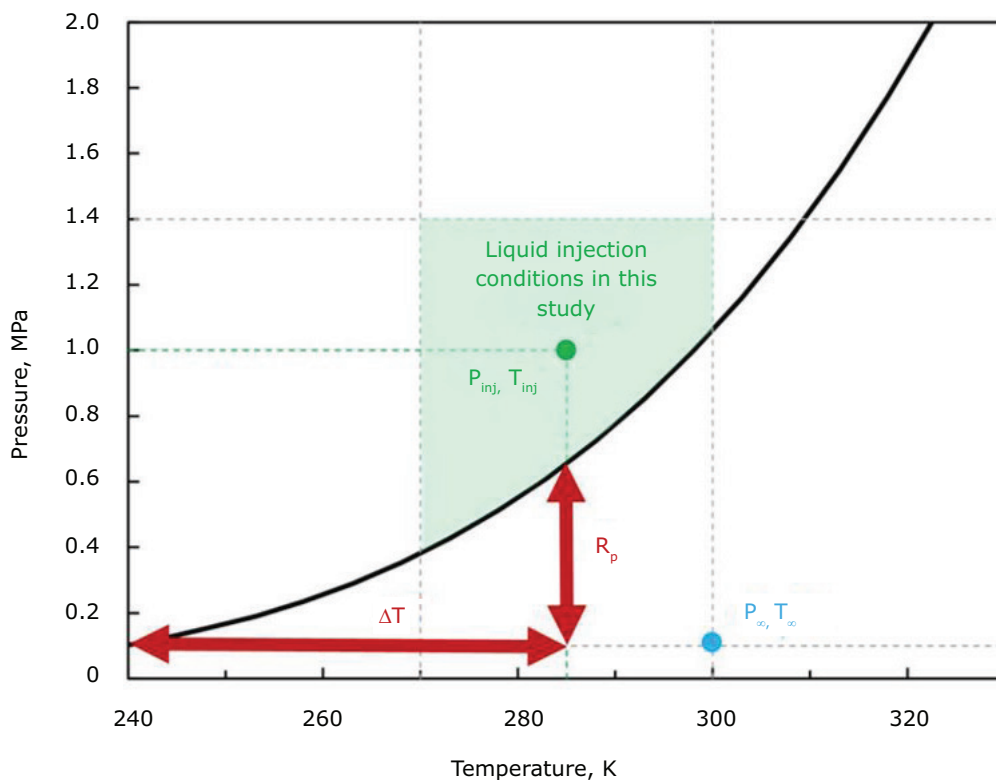


Fig. 4. Ammonia liquid-vapour phase change. Reprinted from (17) with permission from Elsevier

the introduction of gasoline direct injection (GDI) have provided a route for the advancement of this technology for ammonia utilisation.

Aside from combustion applications, large-scale hazardous releases of liquid ammonia have been studied to examine issues relating to atmospheric dispersion and toxicity. The safety aspects of storing and transporting ammonia in large quantities are very well known, though large-scale releases clearly provide additional complications both in terms of computational modelling as well as experimental validation (13, 14). Nevertheless, the underlying physical processes should be consistent

between fuel injection for propulsion applications and accidental atmospheric dispersion, under comparable initial or boundary conditions.

The physical properties of ammonia are similar to propane, with both fuels easily stored as a pressurised liquid and with a resultant high energy density when compared to their gaseous form. Both propane and ammonia are commonly used as the working fluid in refrigeration cycles due to their relatively high latent heats of vaporisation, of 428 kJ kg^{-1} and 1369 kJ kg^{-1} respectively. The physical properties of ammonia: boiling point of approximately 239.8 K at 1.013 bara (1 atm)

pressure and a vapour pressure of 10.0 bara at standard ambient temperature (298.15 K), mean that similarly to propane, it is relatively straightforward to store and transport the chemical.

Compared to conventional liquid fuels, the vapour pressure characteristics of ammonia result in additional complexities that need to be considered when evaluating the method by which atomisation occurs. The boundary conditions, i.e. the pressure and temperature of both the ammonia and the environment into which it is being introduced, need to be related to the liquid boiling properties to evaluate how the thermodynamic and ‘mechanical breakup’ processes interact. This contrasts significantly with the established understanding of the atomisation of more traditional fuels, which are primarily governed by ‘mechanical breakup’ in which the aerodynamic and surface tension forces within the jet compete. Different authors use different terminology to describe a thermodynamically unstable jet release (15, 16), but essentially the process involves a metastable liquid jet as it transitions between pure liquid and gaseous states.

Generally, the most influential characteristic of a liquified jet release is the degree of superheat, which can be represented either in terms of the temperature or pressure conditions of the fluid at release (13, 16) i.e.:

$$\Delta T = T_{inj} - T_{sat}(P_{\infty}) \tag{i}$$

or

$$R_p = P_{sat}(T_{inj}) / P_{\infty} \tag{ii}$$

When considered in terms of temperature, the degree of superheat, ΔT , is the difference between

the liquid injection temperature, T_{inj} , and the saturation temperature of the liquid at the ambient pressure conditions, $T_{sat}(P_{\infty})$. If considered in terms of pressure, the degree of superheat, R_p , is the ratio between the saturation pressure of the liquid at the release temperature, $P_{sat}(T_{inj})$, and the ambient pressure condition, P_{∞} . For most of the controlled release scenarios of liquid ammonia, the subsequent liquid jet rapidly boils producing a two-phase flow. The dynamics of two-phase releases have been extensively studied from a hazard viewpoint, in order to develop droplet-size correlations and validate dispersion models (18). More recently, more intricate models are being developed specifically to represent the changing forces and energies acting within superheated ammonia releases (19).

Depending on the ambient environment conditions, the introduction of a liquid phase can result in the ‘flash boiling’ or ‘flashing jet’ phenomena, as the jet converges towards thermodynamic equilibrium. This process is applicable for many liquid fuels and various injection technologies under suitable thermodynamic conditions, for example, the use of gasoline has been shown to ‘flash’ in a direct-injection spark-ignition engine at certain load conditions (20). This phenomenon is prevalent for fluids with low boiling points. For fluids (in this case ammonia), releases may therefore be split into three main categories: (a) vapour release; (b) non-flashing liquid release; and (c) flashing liquid release. Flashing jets, such as those associated with an ammonia release, have become better characterised since the pioneering characterisation study of Kitamura *et al.* (16).

Figure 5(a) and **5(b)** respectively show photographic images and a graphical representation

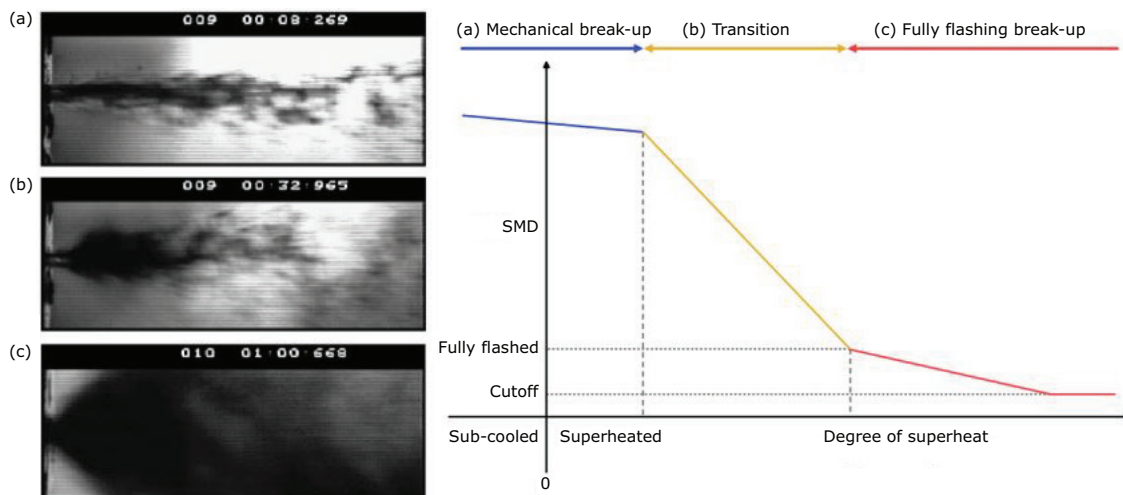


Fig. 5. (a) High-speed imaging of jet breakup modes with increasing superheat (13); (b) Correlating Kitamura jet-breakup to spray quality through tri-linear model (Recreated from (18))

of particle Sauter mean diameter (SMD) vs. superheat for the three main stages of jet breakup identified for a release from a simple orifice (13) following the methodology of Kitamura. For Category A, the jet breaks up with very little evidence of boiling processes. This occurs for releases with little or very low degrees of flashing, or superheat, with this category considered to be dominated by 'mechanical' jet breakup. Mechanical breakup occurs based primarily on the competition between aerodynamic forces, serving to separate liquid fuel into smaller geometries, with the opposing surface tension forces binding the liquid together. Correlations representing this category of breakup are governed by the established non-dimensional parameters such as Weber, Ohnesorge and Reynolds numbers. For Category A releases, the atomisation process involves ligaments and globules being stripped from the surface of the jet, which then in turn breakdown to finer droplet throughout the later stages of the atomisation process.

Category B releases occur when there is a significant degree of flashing, or superheat, with external jet breakup through bubble expansion clearly evident, occurring a short distance from the orifice. Category C releases occur at the highest degree of flashing, or superheat and produce a fully broken-up spray dominated by bubble nucleation and micro explosions. Nucleation invariably commences upstream of the orifice exit, sometimes causing issues concerning stability of upstream flow through vapour locking or injector deterioration. Transition between the different modes of flashing jet breakup is governed by thermodynamic processes, represented by dimensionless groups such as the Jakob number, Weber number and liquid/ vapour density ratio. Fully flashing jets are highly dynamic atomisation processes, accompanied by significant turbulence generation and air-entrainment, which are of great relevance to producing readily combustible mixtures.

More recently, Li *et al.* (21) re-appraised the phenomenology of flashing ammonia jets in the context of reciprocating engines. Near-field bubble explosion characteristics were correlated with the measured far field tip penetration. Similar to the atmospheric dispersion studies, they concluded that flashing (or superheated) ammonia sprays can be divided into an initial flashing region ($1.0 < R_p < 2.0$), a transitional flashing region ($2.0 < R_p < 5.0$) and what they termed 'flare flashing' for $R_p > 5.0$. A non-dimensional analysis

was established to correlate critical features. The observed bubble explosion intensity in the near field was dominated by the degree of superheat and fuel viscosity over the entire flashing region, while the Ohnesorge number was more influential in the transitional flare regions. The tip penetration presented similar characteristics to conventional liquid fuels under critical and initial flashing conditions, whereas jet bubble behaviour dominates penetration under transitional and flare flashing conditions.

Colson *et al.* (17) developed the phenomenology of flashing (ammonia) sprays, building upon the earlier phenomenological models of Kitamura *et al.* (16) and Cleary *et al.* (13). Liquid ammonia sprays were observed using high speed backlit imaging for a range of superheat values between 3.5–8.5 for single hole injectors with diameters between 0.1–0.21 mm and additional parameter of injector aspect ratio (L/d) between 2.5–10. Consistent with previous studies, it was found that superheat dominated the transition to flashing, which was also highly dependent upon the injector L/d ratio. Previous transition criteria were not found to correlate well with for the ammonia case for the diameters and aspect ratios investigated. The upstream internal flows of the injector were visualised (**Figure 6**) with results suggesting that increasing the orifice section

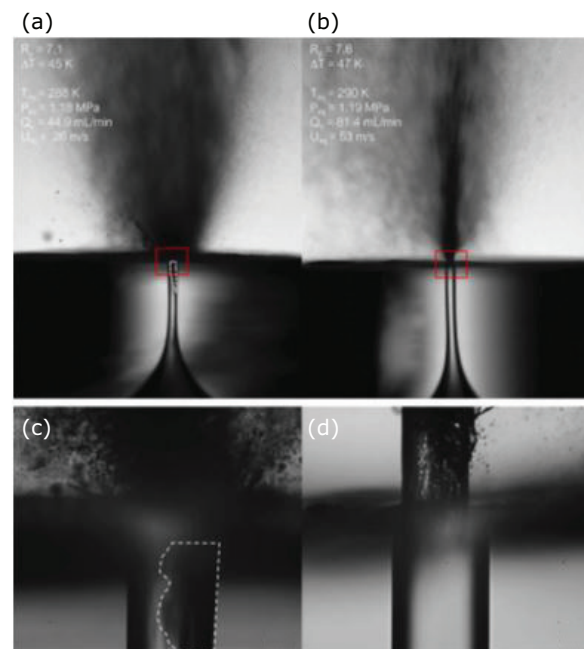


Fig. 6. Effect of small change in the orifice geometry and inner flashing for $L/D = 11$, reprinted from (17) with permission from Elsevier

towards the outlet of the injector could enhance the flashing of the liquid ammonia spray.

3. Characterisation of Ammonia Sprays

3.1 Spray Characterisation

Non-intrusive methods for studying spray diagnostics have developed significantly over the past 40 years. The 1970s and 1980s saw the introduction of high-speed imaging to interrogate global spray parameters such as jet penetration, spray cone-angle and spray morphology. **Figure 7(a)** shows the

basic traditional parameterisation of a non-flashing spray *via* its release orifice dimension, cone angle and overall penetration. **Figure 7(b)** shows a recent utilisation of high speed ‘Schlieren’ imaging to reveal a three-stage propagation behaviour associated with tip penetration for an ammonia jet of 2 ms injection duration, relevant to internal combustion engine applications. Clearly there are application design uses for such diagnostics and simplified correlations.

Pelé *et al.* (23) presented high speed images of liquid and superheated ammonia jets, enabling a comparison of jet penetration for liquid or two-phase ammonia releases into elevated ambient conditions. The Schlieren imaging technique

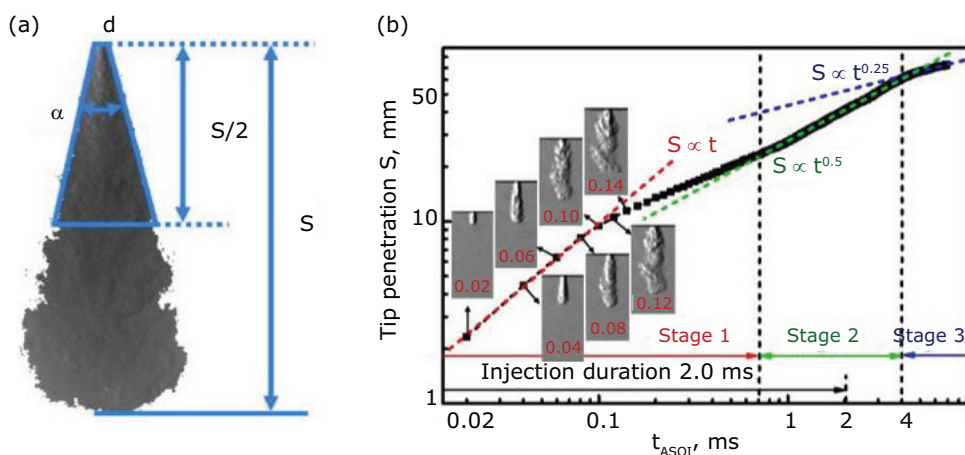


Fig. 7. Three-stage behaviour of the tip penetration of ammonia jets. ($P_{inj} = 8.0$ bar, $P_a = 2.0$ bar, $T_a = 298$ K, $\tau = 2.0$ ms). Reproduced from (22) with permission from Elsevier

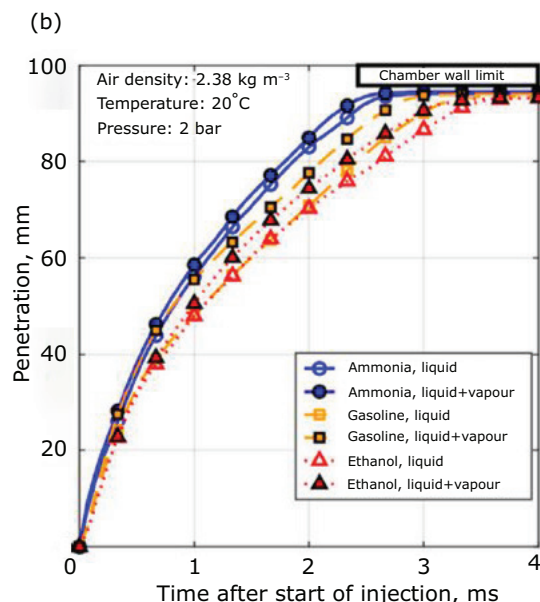
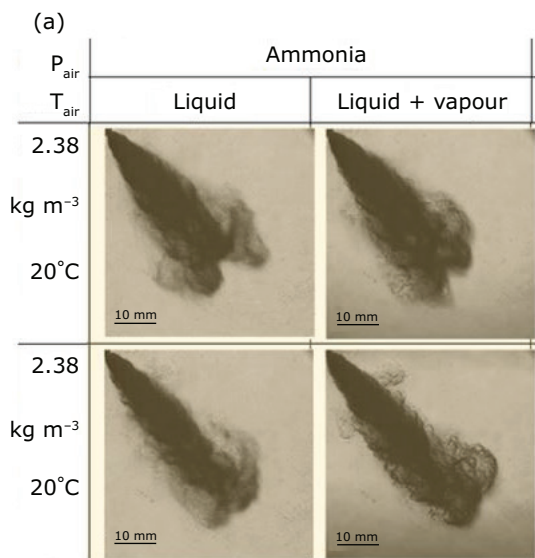


Fig. 8. Comparison of spray penetration for ammonia (continuous line), gasoline (dashed line) and ethanol (dotted line): (a) $T_{air} = 293$ K and $P_{air} = 2$ bar; (b) $T_{air} = 293$ K and $P_{air} = 7$ bar; (c) $T_{air} = 393$ K and $P_{air} = 2.69$ bar; (d) $T_{air} = 393$ K and $P_{air} = 9.39$ bar. Reproduced from (23) under Creative Commons Attribution Licence 4.0 (CC BY)

together with dedicated image post processing enabled identification of the vapour phase relative to the spray boundary. **Figure 8** demonstrates the penetration for liquid and liquid/vapour (23).

The average size of droplets in an established spray is generally described as the spray 'quality' *via* some defined average diameter, such as the SMD for combustion applications (24). The SMD has been identified as generally having a strong influence upon subsequent processes, whether that be the ignition or turbulent flame propagation in the context of internal or external combustion engines, or for non-combustion applications such as the rainout and subsequent pool boiling and re-evaporation for stratified atmospheric releases. Spray quality may also be represented as a distribution of droplet sizes through volume (or number) distributions. The so called 'Rosin-Rammler' distribution function has been often deployed to represent the distribution of droplet sizes in sprays. A range of correlations for droplet distributions and mean droplet sizes have been developed and utilised by researchers for different applications and as such it is important to ensure the correct parameter is used when comparing and evaluating results.

The laser diffraction technique, primarily a line-of-sight technique, was one of the first non-intrusive laser-based particle sizing techniques developed to measure droplet sizes and is still used extensively today. Subsequently, more complex non-intrusive laser techniques have been developed enabling considerably more detailed spatial and temporal characteristics to be unveiled, which in turn has led to the development of more intricate modelling subroutines which are then validated against experimental data. Two techniques have prevailed in terms of spray flow field kinematics: laser doppler anemometry (LDA) and particle imaging velocimetry (PIV). LDA is an absolute method which relies on measuring the frequency of Doppler bursts produced when droplets pass through an optical fringe control volume to evaluate the components of the velocity at a point in space, whereas PIV relies on the visual interrogation of sequential imaging with dedicated post processing to track particle velocity components that have been illuminated within the flow field.

Depending on the application, different techniques have been developed to enhance the basic spray diagnostic techniques outlined above. For example, transient multidimensional diagnostics are desirable for engine applications. This has resulted in the development and widespread utilisation of

full flow-field temporal development of sprays, such as phase-resolved phase doppler anemometry (PDA). This has proven robust and highly valuable for the development of non-flashing direct injection (for example, GDI) sprays. The other diagnostic, which is more challenging, is that of quantifying the vapour phase or both liquid/vapour phases independently (25). Various permutations of laser-induced fluorescence principles have been deployed for spatial and temporal phase resolution, with varying degrees of success.

3.2 Influence of Operational Ammonia Spray Parameters

The boundary conditions used for the characterisation of ammonia sprays depend upon the particular application. Reciprocating engine applications rely on dedicated, well-established industry-specific fuel injector technology and detailed proprietary atomiser designs, whereas hazardous atmospheric releases are a function of the operational control conditions and variable release orifice shape. Hence, while a fuel injector and its operational control parameters (mass flowrate, release pressure) can be carefully designed and engineered, atmospheric releases are generally idealised from a potential sharp-edged, non-geometric shaped orifice characteristic of a containment rupture or leak.

Concerning the 'ambient' boundary conditions, reciprocating engine applications need to consider injection into potentially elevated pressure or temperature environments, depending upon the particular fuelling strategy being deployed. Additionally, reciprocating engine applications can utilise a range of injector durations, injector pressures (**Figure 9**) and even multiple injection strategies, which can have variable times of injection during the engine stroke, changing the 'ambient' boundary condition. Hence, a number of dedicated optical rigs for spray characterisation have been designed by various research groups over the past 30 years, as shown in **Figure 10** (18, 23), which have included suitably specified optical access for the variety of non-intrusive analytical techniques previously described.

The work of Fang *et al.* (26) included an investigation of high-pressure liquid ammonia injections at pressures up to 1000 bar under both non-flash and flash boiling conditions. Results from this work, an example of which is shown in **Figure 11**, compares the penetration rates observed in their high-pressure vessel against

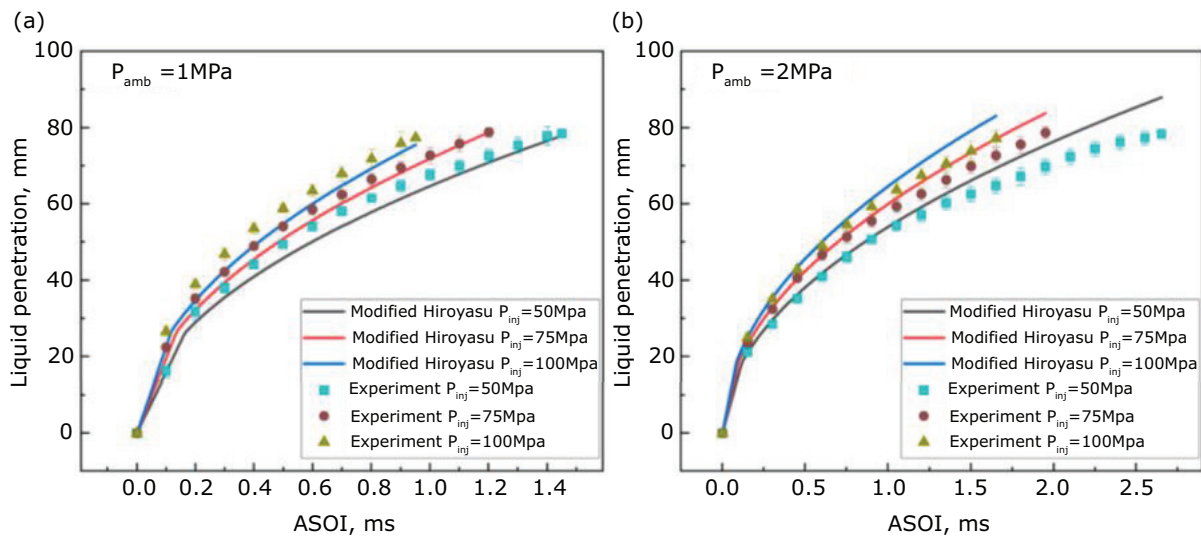


Fig. 9. Influence of P_{inj} upon liquid penetration. Reproduced from (26) under Creative Commons Attribution Licence 4.0 (CC BY)

established empirical models (Hiroyasu *et al.* (28), Naber and Siebers (29)). The flash boiling condition identified a suppression of spray penetration during the early stages and was named the ‘spray resistance phenomenon’, observed when P_{amb} was less than 7 bar and found to be highly correlated to the degree of superheat. The reason attributed to the spray resistance is injector needle lift leading to cavitation upstream of the exit orifice (16, 18) which results in an undesirable injector blockage due to vapour generation. The requirement to eliminate or suppress strong vapour generation within the nozzle is emphasised, such that the design of an ammonia fuel delivery system is more challenging as it is not simply a case of generating fully flashing sprays.

4. Modelling Ammonia Sprays

Numerical computational methods have been utilised and developed to model the formation of ammonia jets or sprays and the propagation of a flame throughout dispersed droplet fields. Recently Zembi *et al.* (27) developed and ‘tuned’ a commercial CFD numerical model, incorporating the RNG- $k\epsilon$ turbulence model, to provide a detailed simulation of both a flashing and non-flashing spray, validated against accompanying experimental data. Schlieren imaging was utilised to identify the spray and vapour boundaries for validation, while laser diffraction was utilised to generate line of sight SMD. The fuel injector utilised was a contemporary Bosch GDi unit comprising seven holes of 150 μm

diameter. The authors found that validated global spray characteristics were readily obtained for the flashing spray, whereas more detailed temporal or spatial resolution for diagnostics such as droplet sizes and vapour mass fraction proved more challenging. An example of their findings is shown in Figure 12. Previous work has drawn similar conclusions using a pressure-swirl GDI injector (30).

Figure 13 shows the significant variation in the predicted vapour mass fraction between the flashing and non-flashing sprays using the tuned simulation. Validation of such quantified temporal or spatial diagnostics remain a challenge. Figure 14 shows the difference in SMD for flashing jets, predicting a reduction in SMD from 30–40 μm for the non-flashing case, to below 10 μm for flashing. In terms of combustion, this difference in droplet size distribution would be very influential, as the ‘mode’ of spray combustion changes from diffusion-based droplet-droplet propagation to premixed spray propagation traversing the so-called droplet combustion ‘transition range’ (31). These processes will vary and may be diminished, within the high pressure or high temperature engine injection environments, but the modes should still appear and depend primarily on spray quality.

Zembi *et al.* (27) also modelled another influential effect of flashing jets: namely the temperature reduction of the environment due to flash boiling (Figure 15), a result of the large heat of vaporisation of ammonia. These are very significant reductions which in reciprocating engines can be

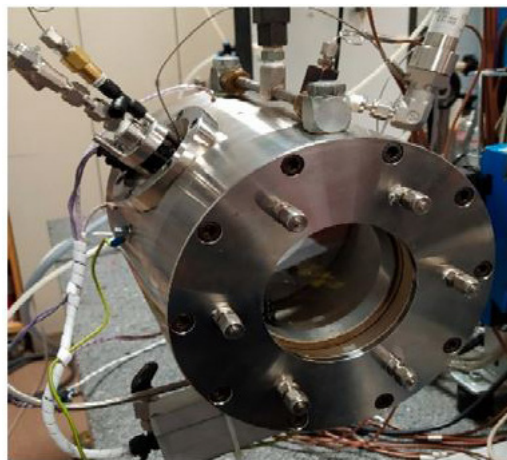
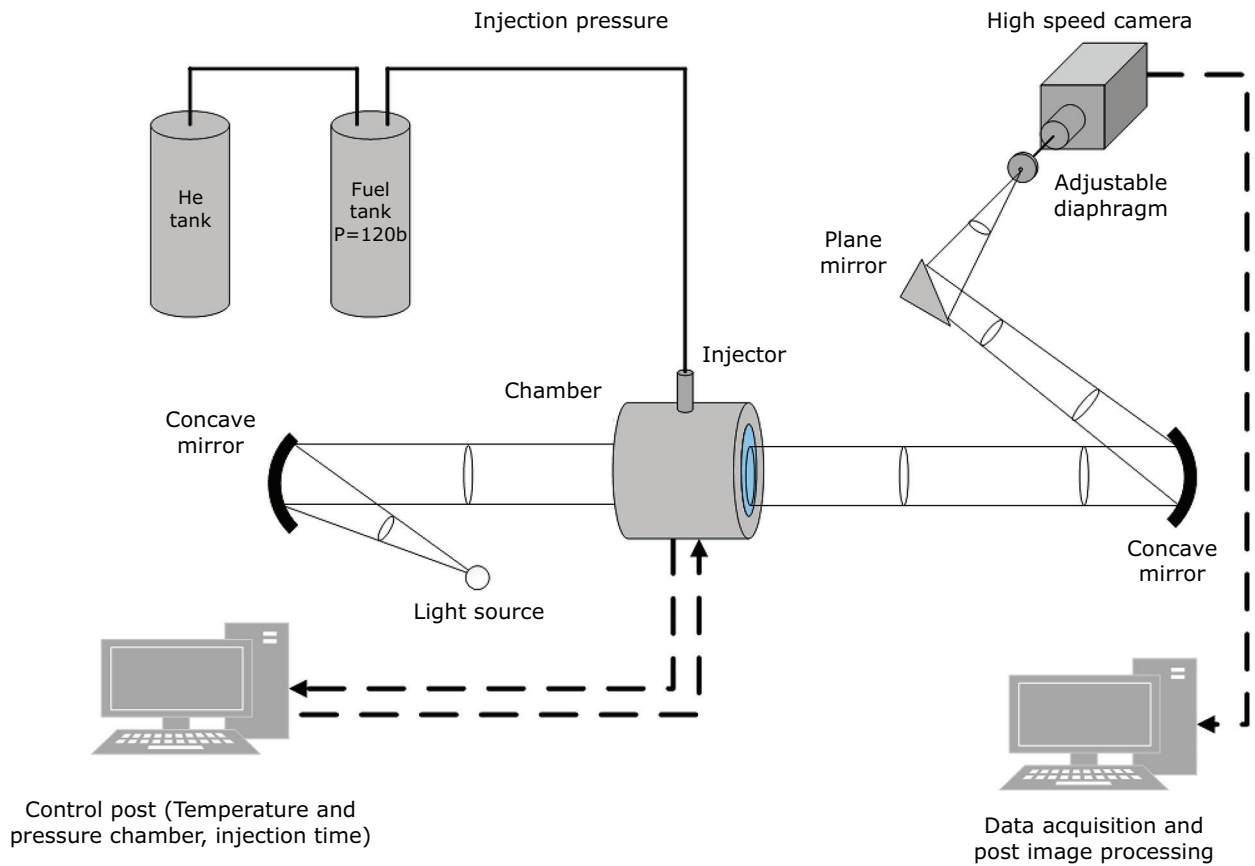


Fig. 10. Experimental apparatus used by various authors to study ammonia spray characteristics for a GDI engine injector. Reproduced from (23, 27) under Creative Commons Attribution Licence 4.0 (CC BY-NC-ND)

utilised to enhance charge cooling, which has the potential for allowing for an increase in the physical compression ratio of the engine or a reduction in the peak cylinder temperatures, possibly resulting in an increase in overall efficiency or providing a mechanism for reducing NO_x formation.

An *et al.* (12) studied, *via* numerical means, the combustion and spherically expanding flame propagation characteristics in a dispersed

droplet field. The primary goal of this work was to compare liquid ammonia spray flames to the gaseous equivalent. Simulations of the spherically expanding flames were performed using the Eulerian-Lagrangian framework, where the Lagrangian method is used to capture droplet dynamics. Liquid ammonia spray simulations have been extended to reacting flows, where two-way coupling enables gas and droplet interactions (32).

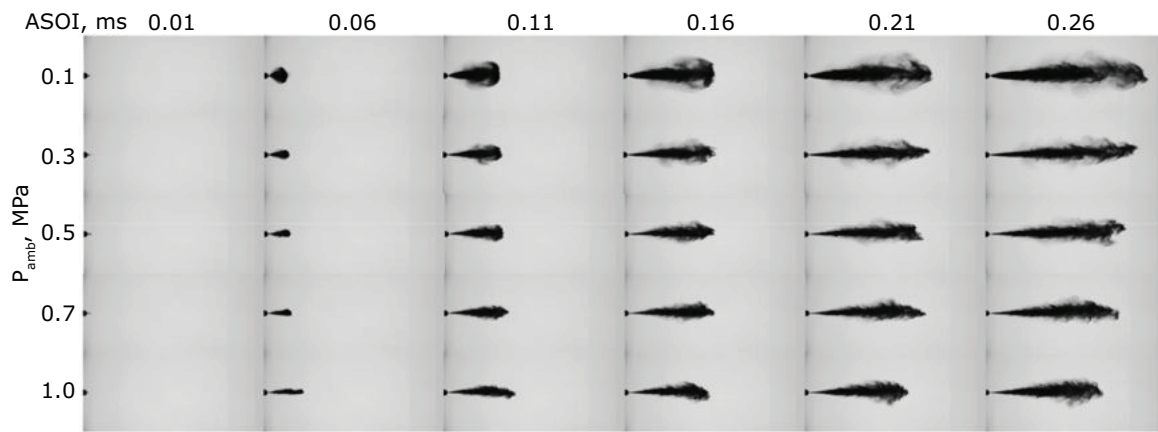


Fig. 11. Influence of ambient pressure on transient flashing ammonia jet morphology. Reproduced from (26) under Creative Commons Attribution Licence 4.0 (CC BY)

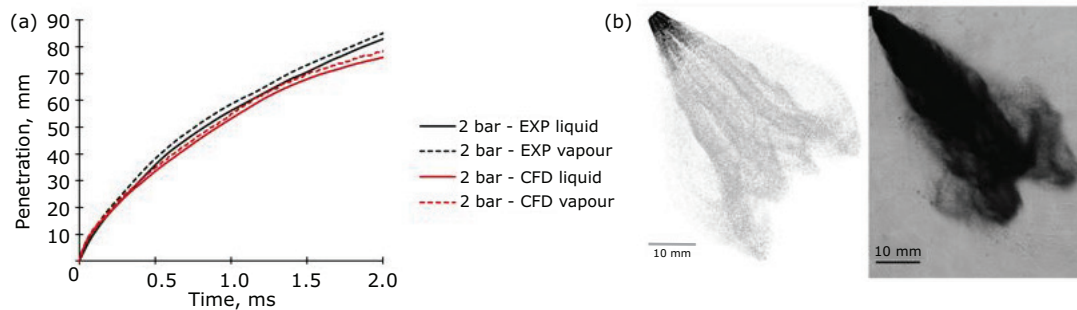


Fig. 12. Comparison between experiments and simulation in terms of penetration: (a) and spray morphology; (b) for flashing ammonia spray. Reproduced from (27) under Creative Commons Attribution Licence 4.0 (CC BY-NC-ND)

It was concluded that the presence of ammonia droplets significantly reduces the flame propagation speed and heat release due to the local heat loss caused by flash boiling. Preheating was found to be highly influential when it comes to ignition, while the liquid ammonia droplet suspension could not be ignited at normal (in this case 300 K) temperatures without preheating. Competition between the heat generated by the chemical reaction and the heat absorbed by the phase change was found to be the dominant factor when it comes to liquid droplet ammonia ignition. Smaller droplets were found to evaporate quickly, significantly reducing the temperature and increasing local mixture fraction, whereas flame-droplet interaction was more dominant for cases of large droplet diameter, with local heat loss near the larger droplets causing local extinction. Regarding equivalence ratios and heat fractions, the flame propagation characteristics were found to be dependent on the proportion of

liquid ammonia and therefore the local evaporation rate, resulting in different levels of heat loss. Stoichiometric conditions were no longer predicted to be the most suitable for ignition.

5. Ammonia Sprays for Combustion Applications

Early work undertaken by Verkamp *et al.* (10) supplied ammonia in both liquid and gaseous phases to a gas turbine combustor. The work summarised that ammonia could only be accommodated in conventional gas turbines when supplied in the gaseous phase to ensure flame stability and that the diameter of the combustor liner would consequently need to be increased by a factor of ~ 2 . However, in later work by Okafor *et al.* (33) an improved understanding together with technical developments meant that a 230 kW gas turbine combustor could be successfully

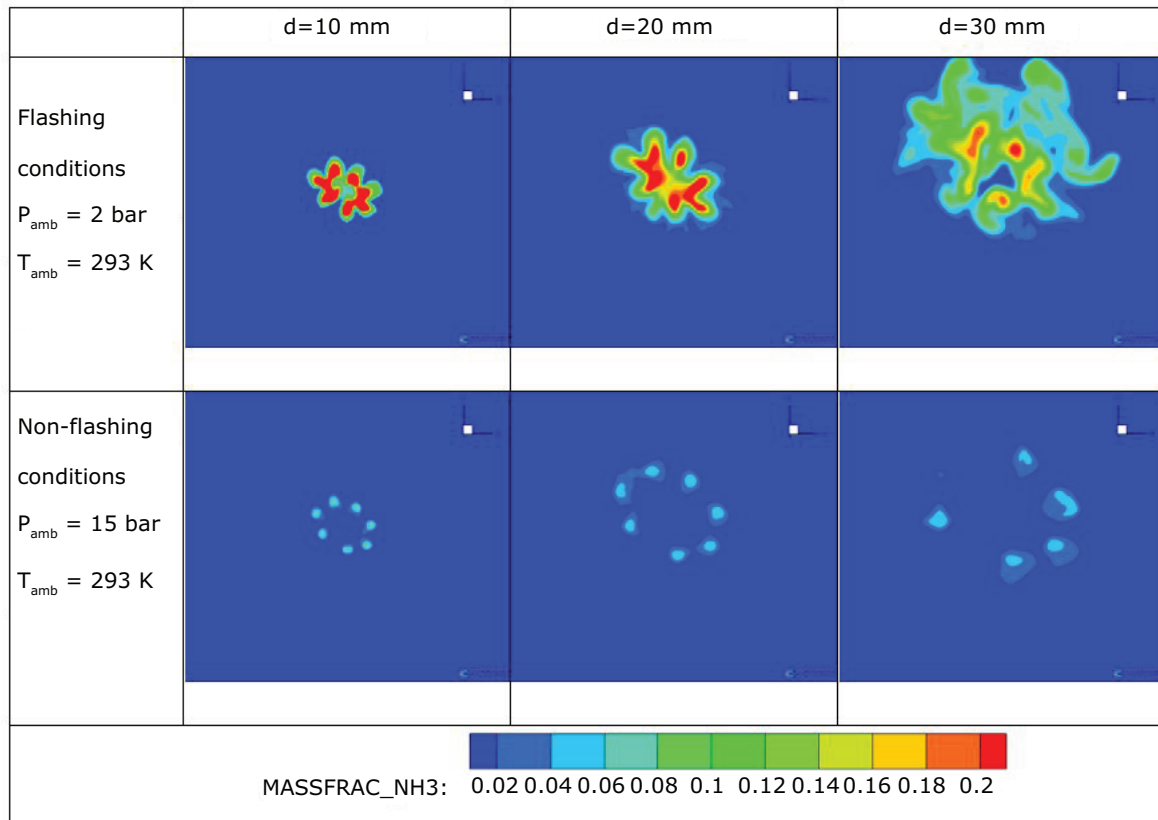


Fig. 13. Ammonia vapour mass fractions for flashing and non-flashing jets (simulated). Reproduced from (27) under Creative Commons Attribution Licence 4.0 (CC BY-NC-ND)

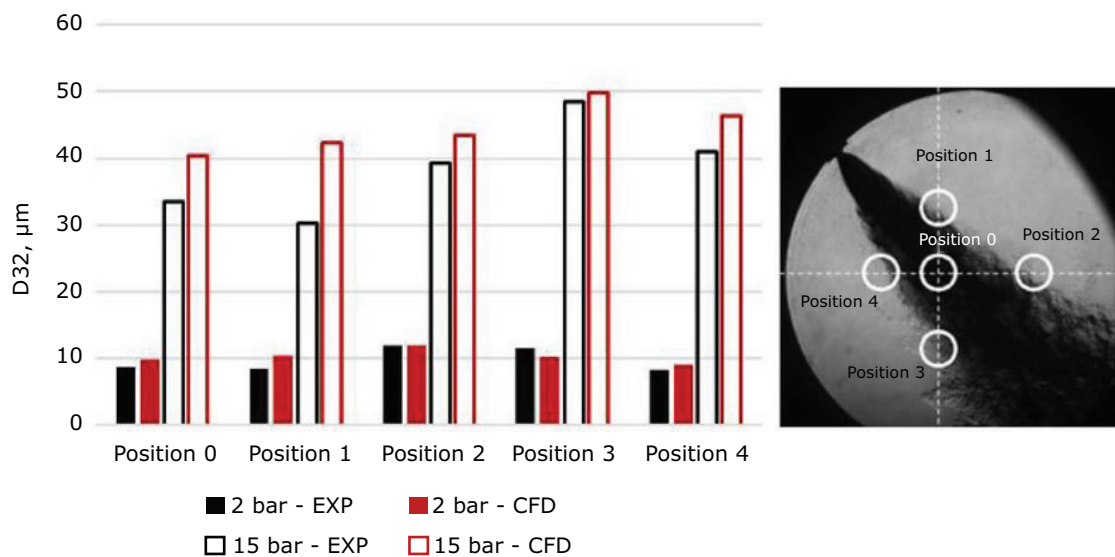


Fig. 14. Comparison between experiments and simulation in terms of local SMD - flashing (2 bar) vs. non-flashing (15 bar). Reproduced from (27) under Creative Commons Attribution Licence 4.0 (CC BY-NC-ND)

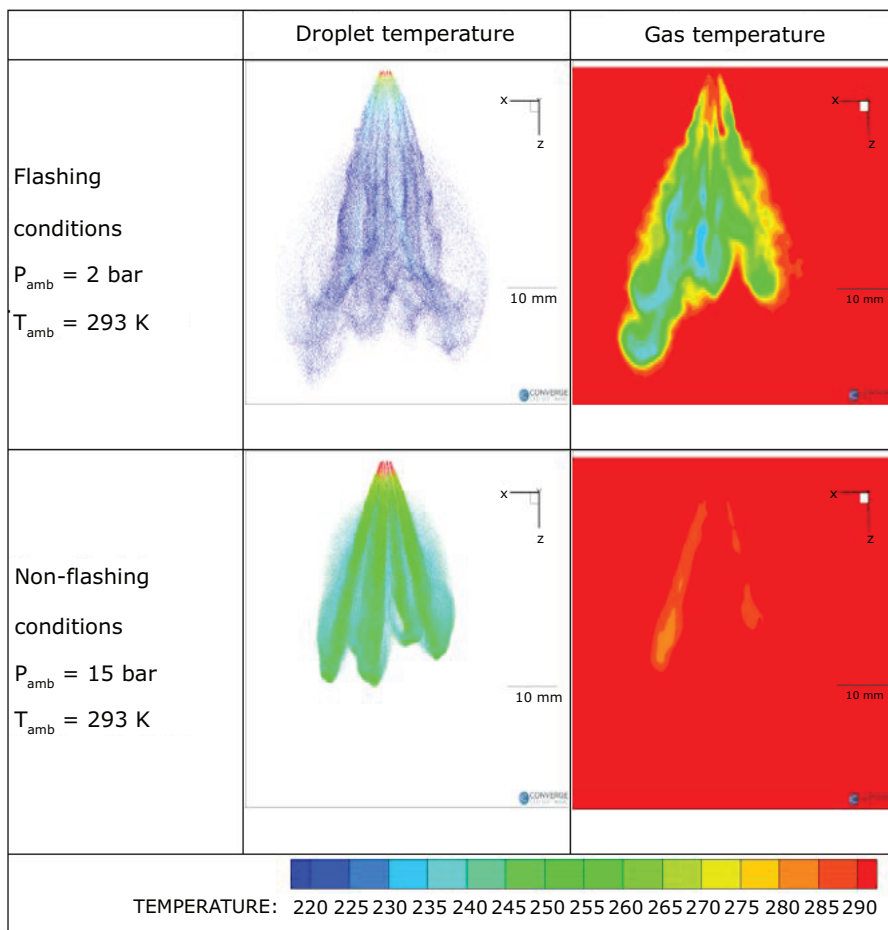


Fig. 15. Simulations of droplet and gas temperatures flashing and non-flashing sprays 1 ms ASOI. Reproduced from (27) under Creative Commons Attribution Licence 4.0 (CC BY-NC-ND)

operated with a staged liquid ammonia flame. Rich-lean staged liquid combustion was stated to be advantageous, since it can allow for significant reduction in NO_x, nitrous oxide and unburned ammonia emissions over single staged combustors and mitigates the need for larger combustor geometries.

The work studied the effects of co-firing methane, alongside changes in wall temperature, on flame stability. The authors suggest that sufficient compensation for heat extracted from droplet vaporisation is necessary to improve efficiency in the primary combustion zone and thereby reduce the quantity of unburned ammonia that is oxidised in the secondary zone, something that is also important for the control of nitrous oxide emissions from the liquid spray flame. The conventional application of wall cooling in gas turbines was shown to contribute to flame extinction *via* blow-off together with higher nitric acid, nitrous oxide and unburned fuel emissions and operating the system without wall cooling enabled an increase in wall temperature up to 1273 K, facilitating

the stabilisation of the liquid ammonia spray (**Figure 16**).

Okafor *et al.* (34) also conducted liquid ammonia trials in a novel swirl combustor co-fired with methane. PIV was used to measure the non-reacting air flow field and the ammonia spray was visualised by Mie scattering. The work concluded that stable combustion of liquid ammonia was ensured by cooling the liquid ammonia to avoid evaporation in the supply line and also reduce cavitation in the spray nozzle. The addition of methane further improved flame stability and the overall combustion efficiency. However, the system still produced excessive emissions of nitric acid, carbon monoxide, hydrogen cyanide, hydrogen and ammonia, depending on the employed equivalence ratio.

Recent reciprocating engine studies, focused on marine engine applications, have considered dual fuelling of ammonia with a diesel pilot, using numerical and experimental analysis. Scharl and Sattelmeyer (35) utilised a rapid compression-expansion machine (RCEM) to examine single

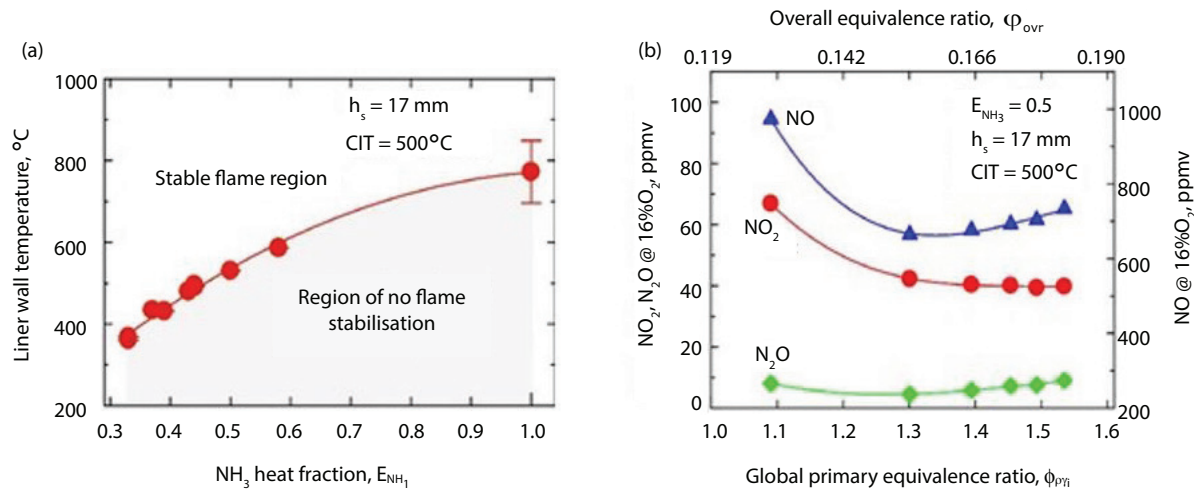


Fig. 16. (a) Blow-off limits based on ammonia heat fraction and liner wall temperature, showing the extension of the stable flame regions to pure liquid ammonia combustions; (b) variation of nitric oxide, nitrogen dioxide and nitrous oxide emissions with equivalence ratio at 50% ammonia heat input. Reprinted from (33) with permission from Elsevier

ammonia sprays interacting with small diesel pilots at engine relevant conditions. The spatial and temporal interaction of the two sprays was enabled by a controlled variation of the interaction angle and the relative injection timing. It was found that the reliable ignition of ammonia was possible using a pilot with a lower heating value (LHV) fraction as low as 3.2%, with the ignition delay increasing for smaller (diesel) pilot quantities. Shorter, high mass flux, pilot injection durations were found to reduce ignition delay and accelerate the onset of ammonia combustion. The paper concludes that high-pressure dual fuel combustion of ammonia is feasible in real engines and that development of multi-jet engine injectors is advocated. Also, due to the absence of real engine design features within the RCEM, real engines could perform significantly better than expected on the basis of the results presented.

Zhou *et al.* (36) undertook CFD simulations of low speed, duel fuel, pilot diesel-ignited ammonia marine engines, to compare ammonia premixed and high-pressure spray combustion modes. The Euler-Lagrangian numerical model predictions for both modes of operation were verified against experimental data such as spray mixture formation and ignition delay. The engine performance and emissions of both modes are optimised, leading to the conclusion that indicated thermal efficiencies of over 50% can be achieved for both modes. The optimised ammonia high-pressure spray combustion point can achieve a similar indicated

thermal efficiency while exhibiting a reduction in the NO_x emissions of around 47% when compared with the diesel-only mode. For both the optimum points, the equivalent total greenhouse gas emissions (i.e., CO₂ + 300 × N₂O) were predicted to be reduced by around 97%, while the unburned ammonia emissions are calculated to be negligibly small.

Very recently, An *et al.* (37) performed numerical simulations using flamelet-based models for turbulent liquid ammonia combustion under flashing conditions. A three-dimensional point-particle direct numerical simulation (PP-DNS) with detailed chemistry was first performed for a liquid ammonia methane cofired flame, revealing three distinct regions in the combustion: (a) a mixing stage; (b) methane-dominated combustion stage; and (c) fully reacting combustion stage. Heat release from methane-dominated combustion served to counter heat loss by the simultaneously flashing liquid ammonia droplets, effectively acting as a 'pilot' flame before ignition of the vaporised ammonia. Using the DNS results as a baseline, three flamelet-based models were compared: the extended flamelet-progress variable (E-FPV), extended flamelet-generated manifolds (E-FGM) and extended hybrid (E-Hybrid). It was found that the E-FGM model provided the best agreement with DNS results, as it was able to better capture the rapid flash evaporation and mixing of the liquid ammonia and was therefore the best suited for future simulation of liquid ammonia combustion and liquid ammonia and methane co-fired flames.

6. Future Trends

Future trends concerning ammonia life cycle assessment will include a steady adoption of near-zero emission technologies, with an increase in both the use of carbon capture and storage as well as electrolysis at the production stage. By 2050, green ammonia production is predicted by the International Energy Agency to make up more than 40% of the worldwide demand (38). Due to its convenient thermodynamic properties, it is anticipated that the use of ammonia in diverse sectors of industry, transportation and power generation will develop quickly while optimum systems for implementing ammonia-based fuels will rapidly mature.

The marine sector seems likely to be an early adopter of ammonia for propulsion, as evidenced by the joint efforts of Yara Clean Ammonia, North Sea Container Line and Yara International towards development of an ammonia powered container ship by 2030 (39). Separately a Japanese consortium comprising Nippon Yusen Kabushiki Kaisha, Japan Engine Corporation, IHI Power Systems Co and Nihon Shipyard Co Ltd has been formed with the aim of constructing the world's first ammonia-fuelled medium gas carrier, due for completion at the end of 2026 (40). As increasingly large quantities of liquefied ammonia will be transported to global markets by sea, using the product as a fuel in parallel seems an obvious corollary. Shipping is currently the most efficient means of transportation for limiting CO₂ emissions per metric tonne-kilometre, being 25 times more efficient than air freight and 2–3 times more efficient than rail freight (41). However, there are currently no commercial ammonia fuelled engines for shipping and there remain challenges for power-plant designers before fully optimised ammonia-fuelled engines can be deployed. One important aspect concerns the optimisation of ammonia fuel-injection systems in relation to efficiency improvements and pollutant, particularly NO_x, reduction.

Parametric optimisation of fuel injection initial and boundary conditions will be enhanced by new empirical correlations suitable for engine system relevant conditions. This will be underpinned by fundamental experimental data, of which there is currently a lack of with regards to ammonia specific energy conversion systems. The University of Oxford's AmmoSpray project aims to address this by providing step-by-step fundamental data on the characteristics of ammonia sprays at combustion

relevant conditions (including liquid breakup), towards better understanding of the link between ammonia sprays and combustion behaviour. Also, multi-fuel injection is likely to become more prevalent, to overcome ammonia reactivity issues. Research into ammonia fuel injection will require further experimental temporal and spatial resolution to enable appraisal and enhancement of contemporary simulations. Contemporary optical diagnostic techniques, for the large part, are capable of providing such data, though new techniques to quantify mixedness, for example, will be pursued. Numerical techniques will be developed and deployed to provide more efficient and accurate simulation of free surface problems such as ammonia sprays. Engine research design centres, fuel spray combustion fundamentalists and manufacturers will work more closely together to ensure timely ammonia power-plant development, leading to significant contribution to the global net zero carbon goals and aspirations. This is a key aim of the recently started MariNH₃ research programme.

A variety of concepts and ideas have been put together over the previous sections, each of which have important paths towards further development and progression. This has significance for the practical application of ammonia mixtures, with a specific requirement for investigations at engine and system relevant conditions. There will also be enhanced work in the field of improving ammonia flame stability, with scope to increase the maximum achievable fraction of ammonia in fuel sprays. This may require enhancements to both reactant and combustor ambient temperature and under such conditions, NO_x formation presents a significant barrier to the wider implementation of pure ammonia as a future zero-carbon fuel. It is a crucial challenge for researchers to develop and employ advanced combustor concepts with ammonia while ensuring the NO_x emissions meet relevant standards.

7. Conclusions

Ammonia is a zero carbon, combustible and internationally transported chemical, which liquifies at modest thermodynamic conditions enabling ease of transportation. However, ammonia combustion kinetics are generally slow, giving rise to a comparatively high ignition energy and low burning rates. Excessive NO_x production is another major inhibitor and challenge moving forward. Liquid fuel injection has the potential

to enhance ammonia combustion performance across a range of heat, power and propulsion applications, including burners, boilers and engines.

Over the past five years, literature concerning releases of ammonia jets for combustion applications has developed rapidly, alongside global world-wide interest in utilising ammonia as an energy vector, led by countries including Japan, UK, France, China, Saudi Arabia and Australia.

Due to ammonia's thermophysical properties, liquid fuel injection systems must be carefully designed to achieve the desired liquid, vapour or mixed liquid/vapour injection conditions. There are significant thermodynamic differences associated with high volatility fuels with phase-change potential such as ammonia, butane and propane, compared with stable traditional hydrocarbon liquid or vapour fuels.

Liquid ammonia injection can result in the so-called 'flash boiling' or 'flashing jet' phenomenon. This has been studied and analysed in the context of combustion applications as well as accidental releases of superheated toxic materials.

To date, engine researchers have mainly utilised previously designed bespoke optical rigs, together with established advanced optical diagnostics and multi-phase numerical models. This has resulted in ammonia-specific trends for global spray characterisation being produced and contrasted with those previously designed and utilised for fuel injection of a thermodynamically stable hydrocarbon fuel.

Non-flashing jets may be characterised *via* the established phenomenological model representation of primary and secondary atomisation, coupled with oxidant entrainment, prior to combustion. For 'flashing' or 'flash boiling' jets, the degree of superheat together with the injector design dimensions are highly influential in characterising these sensitive jets. Critical transitional conditions have previously been correlated empirically by utilising non-dimensional thermofluid analysis groups, including Reynolds, Weber, Ohnesorge and Jakob numbers. For ammonia applications, correlations concerning spray quality have been proposed, though validation is currently limited.

Several studies have employed numerical schemes for studying ammonia liquid sprays, with frameworks developed from characterising sub-cooled liquid hydrocarbon sprays. Spray/jet characterisations have mainly concentrated on global, yet influential, diagnostics parameters such as penetration and spray angle. Few studies have explored spray quality

(mean particle sizes or distributions) and none in a detailed spatial-temporal sense which would enable parallel CFD validation or enhancement for reciprocated engine simulation.

Original characteristics and empirical correlations in terms of tip penetration and spray angle have been proposed. Similarities have been reported for penetration (such as three-stage tip penetration), cone angle and fuel mole fraction of ammonia compared with methane on the spray central axis and tip penetration correlations have been generated for several initial and boundary conditions. A so called 'spray resistance phenomenon' has been identified for internally flashing jets, decreasing the mass flowrate and tip penetration velocity accordingly with implications for practical devices. The strong cooling effect anticipated due to the large heat of vaporisation has been observed in numerical studies, which potentially provides a significant practical advantage in engines through charge cooling. These influence fuel injection at ambient pressure and temperatures.

Though there has been an accelerating interest measured in research outputs of ammonia spray combustion over the past five years, for both power generation and transport applications, there are still considerable gaps in the literature, which require addressing to enable optimised utilisation of ammonia as a fuel. While a full review of the application of ammonia sprays to internal combustion engines is not in the scope of this study, it is noted that the research presents positive signals for the future of ammonia fuelled systems within the marine sector in particular.

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References

1. "Statistical Review of World Energy", 72nd Edn., Energy Institute, London, UK, 2023, 64 pp
2. A. Valera-Medina, F. Amer-Hatem, A. K. Azad, I. C. Dedoussi, M. de Joannon, R. X. Fernandes,

- P. Glarborg, H. Hashemi, X. He, S. Mashruk, J. McGowan, C. Mounaim-Rouselle, A. Ortiz-Prado, A. Ortiz-Valera, I. Rossetti, B. Shu, M. Yehia, H. Xiao, M. Costa, *Energy Fuels*, 2021, **35**, (9), 6964
3. T. Kandemir, M. E. Schuster, A. Senyshyn, M. Behrens, R. Schlögl, *Angew. Chem. Int. Ed.*, 2013, **52**, (48), 12723
 4. "Global Hydrogen Review 2021", International Energy Agency, Paris, France, October, 2021, 223 pp
 5. L. Lambertz, 'Import of Green Energy: RWE Builds Ammonia Terminal in Brunsbüttel', RWE AG, Essen, Germany, 18th March, 2022
 6. J. Atchison, 'JERA Targets 50% Ammonia-Coal Co-Firing by 2030: Four Critical Ammonia Energy Projects Included in New Funding Announcement', Ammonia Energy Association, Ashburn, USA, 21st January, 2022
 7. 'Mitsubishi Power Commences Development of World's First Ammonia-Fired 40MW Class Gas Turbine System: Targets to Expand Lineup of Carbon-Free Power Generation Options, with Commercialization around 2025', Mitsubishi Heavy Industries Ltd, Tokyo, Japan, 1st March, 2021
 8. 'GE Vernova and IHI Announce next Phase of the Technology Roadmap Aiming to Develop a 100% Ammonia Capable Gas Turbine Combustion System by 2030', General Electric Company, Cincinnati, USA, 24th January, 2024
 9. H. Kobayashi, A. Hayakawa, K. D. K. A. Somarathne, E. C. Okafor, *Proc. Combust. Inst.*, 2019, **37**, (1), 109
 10. F. J. Verkamp, M. C. Hardin, J. R. Williams, *Symp. (Int.) Combust.*, 1967, **11**, (1), 985
 11. J. Shinjo, *Energies*, 2018, **11**, (11), 2971
 12. Z. An, J. Xing, A. L. Pillai, R. Kurose, *Fuel*, 2024, **357**, (A), 129660
 13. V. Cleary, P. Bowen, H. Witlox, *J. Hazard. Mater.*, 2007, **142**, (3), 786
 14. S. Hanna, R. Britter, E. Argenta, J. Chang, *J. Hazard. Mater.*, 2012, **213–214**, 406
 15. M. Xu, Y. Zhang, W. Zeng, G. Zhang, M. Zhang, *SAE Int. J. Fuels Lubr.*, 2013, **6**, (1), 137
 16. Y. Kitamura, H. Morimitsu, T. Takahashi, *Ind. Eng. Chem. Fundamen.*, 1986, **25**, (2), 206
 17. S. Colson, H. Yamashita, K. Oku, K. D. K. A. Somarathne, T. Kudo, A. Hayakawa, H. Kobayashi, *Fuel*, 2023, **348**, 128612
 18. H. W. M. Witlox, M. Harper, A. Oke, P. J. Bowen, P. Kay, *J. Loss Prevent. Proc. Ind.*, 2010, **23**, (6), 831
 19. J. Shin, S. Park, *Fuel*, 2023, **342**, 127841
 20. M. H. Davy, P. Williams, 'The Effects of Flash Boiling on Mixture Formation in a Firing Direct-Injection Spark-Ignition (DISI) Engine', in "Direkteinspritzung im Ottomotor II", ed. U. Spicher, Expert Verlag, Tübingen, Germany, 2000, pp. 154–170
 21. S. Li, T. Li, N. Wang, X. Zhou, R. Chen, P. Yi, *Fuel*, 2022, **324**, (B), 124683
 22. Z. Zhang, T. Li, R. Chen, N. Wang, Y. Wei, D. Wu, *Fuel*, 2021, **304**, 121408
 23. R. Pelé, C. Mounaim-Rousselle, P. Bréquigny, C. Hespel, J. Bellettre, *Fuels*, 2021, **2**, (3), 253
 24. A. H. Lefebvre, D. R. Ballal, "Gas Turbine Combustion: Alternative Fuels and Emissions", 3rd Edn., Taylor & Francis Group LLC, Boca Raton, USA, 2010, 557 pp
 25. M. A. A. Rincon, 'Novel PLIF Techniques for Analysis of G-DI Spray Dynamics', PhD Thesis, School of Engineering, Cardiff University, Wales, UK, 2009, 215 pp
 26. Y. Fang, X. Ma, Y. Zhang, Y. Li, K. Zhang, C. Jiang, Z. Wang, S. Shuai, *Energies*, 2023, **16**, (6), 2843
 27. J. Zempi, M. Battistoni, A. Pandal, C. Rousselle, R. Pelé, P. Brequigny, C. Hespel, *J. Ammonia Energy*, 2023, **1**, (1), 59
 28. H. Hiroyasu, T. Kadota, M. Arai, 'Supplementary Comments: Fuel Spray Characterization in Diesel Engines', in "Combustion Modeling in Reciprocating Engines", eds. J. N. Mattavi, C. A. Amann, Plenum Press, New York, USA, 1980, pp. 369–407
 29. J. D. Naber, D. L. Siebers, SAE Technical Paper 960034, SAE International, Warrendale, USA, 1st February, 1996, 32 pp
 30. M. A. Comer, P. J. Bowen, S. M. Sapsford, S. I. Kwon, *Int. J. Auto. Technol.*, 2004, **5**, (3), 145
 31. P. J. Bowen, L. R. J. Cameron, *Proc. Saf. Environ. Protect.*, 1999, **77**, (1), 22
 32. Z. An, J. Xing, R. Kurose, *Fuel*, 2023, **345**, 128229
 33. E. C. Okafor, O. Kurata, H. Yamashita, T. Inoue, T. Tsujimura, N. Iki, A. Hayakawa, S. Ito, M. Uchida, H. Kobayashi, *Appl. Energy Combust. Sci.*, 2021, **7**, 100038
 34. E. C. Okafor, H. Yamashita, A. Hayakawa, K. D. K. A. Somarathne, T. Kudo, T. Tsujimura, M. Uchida, S. Ito, H. Kobayashi, *Fuel*, 2021, **287**, 119433
 35. V. Scharl, T. Sattelmayer, *Fuel*, 2024, **358**, (B), 130201
 36. X. Zhou, T. Li, N. Wang, X. Wang, R. Chen, S. Li, *Renew. Sustain. Energy Rev.*, 2023, **173**, 113108
 37. Z. An, J. Xing, A. L. Pillai, R. Kurose, 'Evaluation of Flamelet-Based Models for Liquid Ammonia Combustion in a Temporally Evolving Mixing Layer', arXiv:2312.01665 [physics.flu-dyn], 2023
 38. 'Ammonia Technology Roadmap – Analysis', International Energy Agency, Paris, France, 2021,

168 pp

- 39. 'The World's First Clean Ammonia-Powered Container Ship', Yara International ASA, Oslo, Norway, 30th November, 2023
- 40. T. Barlow-Brown, 'Japanese Consortium Signs Contracts for Construction of Ammonia-Fuelled

Gas Carrier', The Royal Institute of Naval Architects, London, UK, 27th January, 2024

- 41. "Alternative Fuels Outlook for Shipping: An Overview of Alternative Fuels from a Well-to-Wake Perspective", White Paper, Bureau Veritas, Courbevoie, France, 4th October, 2022

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