

# Injection characteristics and fuel-air mixing process of ammonia jets in a constant volume vessel

Zhang, Zhifei; Li, Tie; Chen, Run; Wang, Ning; Wei, Yijie; Wu, Dawei

DOI:

[10.1016/j.fuel.2021.121408](https://doi.org/10.1016/j.fuel.2021.121408)

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*Document Version*

Peer reviewed version

*Citation for published version (Harvard):*

Zhang, Z, Li, T, Chen, R, Wang, N, Wei, Y & Wu, D 2021, 'Injection characteristics and fuel-air mixing process of ammonia jets in a constant volume vessel', *Fuel*, vol. 304, 121408. <https://doi.org/10.1016/j.fuel.2021.121408>

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1 Cover page

2 Title:

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4 **vessel**

5  
6 Authors and affiliations:

7 **Zhifei Zhang<sup>1</sup>, Tie Li<sup>1, 2\*</sup>, Run Chen<sup>1, 2</sup>, Ning Wang<sup>1</sup>, Yijie Wei<sup>1</sup>, Dawei Wu<sup>3</sup>**

8 1 State Key Laboratory of Ocean Engineering, Shanghai Jiao Tong University

9 2 Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration

10 Shanghai Jiao Tong University

11 3 Department of Mechanical Engineering, University of Birmingham

12  
13  
14  
15 \*Corresponding address:

16 Tie Li

17 Mulan Building B521, Shanghai Jiao Tong University

18 800 Dong Chuan Rd., Shanghai 200240, P.R. China

19 Tel: +86-21-3420-8348, Fax: +86-21-3420-8348

20 Email: [litie@sjtu.edu.cn](mailto:litie@sjtu.edu.cn)

22 **Injection characteristics and fuel-air mixing process of ammonia jets in a constant volume**  
23 **vessel**

24 Zhifei Zhang<sup>1</sup>, Tie Li<sup>1,2\*</sup>, Run Chen<sup>1,2</sup>, Ning Wang<sup>1</sup>, Yijie Wei<sup>1</sup>, Dawei Wu<sup>3</sup>

25 1. State Key Laboratory of Ocean Engineering, Shanghai Jiao Tong University

26 2. Collaborative Innovation Center for Advanced Ship and Deep-Sea Exploration, Shanghai Jiao Tong  
27 University

28 3. Department of Mechanical Engineering, University of Birmingham

29 **Abstract**

30 The direct-injection of gaseous ammonia is a possible way to fuel engines to meet the scenario of zero-carbon  
31 emission. In this study, for the first time, the injection characteristics and fuel-air mixing process of ammonia  
32 jets are investigated. A Schlieren system is employed to characterize the macroscopic behavior of ammonia  
33 jets including the tip penetration and jet angle. Besides, the fuel concentrations of ammonia jets are  
34 quantitatively measured by LIBS to investigate the fuel-air mixing processes. According to the time evolutions  
35 of jet tip penetration, the three-stage behavior, namely the  $t$ ,  $t^{0.5}$  and  $(t-\tau)^{0.25}$  dependence corresponding to the  
36 early stage of injection, quasi-steady stage and after two times of injection duration respectively, are proposed  
37 and the mechanisms are discussed in detail. The effects of both injection and ambient pressures on the tip  
38 penetration and jet angle, as well as the fuel concentration distributions are investigated. The increased  
39 injection pressure leads to increases in the tip penetration and fuel concentration but decreases in the jet angle.  
40 The effects of ambient pressure are opposite, indicating that the ammonia jet development is governed by the  
41 injection-to-ambient pressure ratio. The comparisons between ammonia and methane jets are conducted. The  
42 results show they have quite similar tip penetrations and jet angles, as well as the nearly equivalent fuel mole  
43 fractions at the jet axis. However, the equivalence ratios in ammonia jets are significantly lower than those in  
44 methane jets, leading to the distinct flammable mixture distributions in ammonia and methane jets.

45 **Keywords:** Carbon-free fuel; Ammonia jet; Schlieren imaging; Tip penetration; Mixing processes.

## 46 **1. Introduction**

47 The main goal of the Paris Agreement unanimously adopted in the Conference of Parties 21 (COP21) in  
48 December 2015 is to hold the increase in the global average temperature to well below 2 °C above pre-  
49 industrial levels [1]. To fulfill the Paris Agreement, it requires decarbonization of energy production by using  
50 carbon-neutral and carbon-free fuels produced from renewable energy. The production of most renewable  
51 energy sources such as wind, tidal and solar energy is intermittent [2]. Hydrogen is a carbon-free fuel with  
52 favorable combustion characteristics and thus is considered to be one of the most promising clean fuels [3].  
53 However, the long-distance transportation and large-scale storage of hydrogen remain unsolved issues, making  
54 it difficult for widespread use, especially for powering mobility purposes.

55 Ammonia is considered as one of attractive carbon-free fuels due to its hydrogen-rich characteristic (up  
56 to 17.8% hydrogen by mass basis) [4]. Moreover, in comparison to hydrogen, ammonia is possible for  
57 liquefaction at room temperature conditions and lower production cost, significantly in favor of storage and  
58 transportation, as well as large-scale production [5]. Nowadays, ammonia has been widely used as fertilizer in  
59 the agricultural sector, refrigerant industrial coolers, and chemical additives for the selective catalytic reduction  
60 (SCR) of the NO<sub>x</sub> emissions in internal combustion engines (ICEs). The utilization of ammonia as a fuel in  
61 vehicle engines can date back to World War II [6]. Due to the lack of diesel fuel in Belgium in 1942, engines  
62 fueled by ammonia have been developed to maintain the bus system. After World War II, the oil supply was  
63 restored, and therefore the researches on ammonia-fueled engines were greatly reduced. In recent years, in  
64 order to moderate the global warming, ammonia-fueled engines have attracted more and more attention around  
65 the world as a promising technology [4, 7, 8].

66 Many literatures have so far reported ammonia's practical application in both the spark-ignition (SI) and  
67 compression-ignition (CI) engines. Compared to gasoline, ammonia has higher octane rating (~130) and thus

68 better anti-knock performance. This provides the potentials to improve the thermal efficiency and output power  
69 of SI engines by achieving a higher compression ratio [9]. More importantly, ammonia-fueled engines can  
70 achieve nearly zero-carbon emission in principle, which complies with the current requirements for  
71 decarbonization. However, the drawbacks of ammonia combustion are characterized by the low laminar  
72 burning velocity, low flame temperature, narrow flammability range, and high resistance to auto-ignition [10-  
73 12], making it difficult to use pure ammonia as a fuel in ICEs. As a consequence, a secondary fuel with good  
74 combustion properties is required to improve the lower combustion intensity of ammonia. Generally, the  
75 combustion promoters employed in the previous studies can be divided into two categories: hydrogen [13-16]  
76 and carbon-based fuels, such as diesel fuel [17-22], gasoline [23-25], dimethyl ether (DME) [26, 27], etc. Since  
77 both ammonia and hydrogen are gaseous under atmospheric pressure, they can be directly mixed and then  
78 introduced into the cylinder by port-fuel injection (PFI), and minor engine modifications are required to  
79 achieve the favorable combustion of ammonia. Many researchers have attempted to employ hydrogen as the  
80 combustion promoter in both ammonia-fueled SI and CI engines. Mørch et al. [9] found that the utilization of  
81 ammonia-hydrogen mixture leads to the higher efficiency and output power compared to gasoline due to the  
82 higher compression ratio. In their study, a fuel mixture with 10% hydrogen by volume fraction provided the  
83 highest efficiency and power. Pochet et al. [14] explored the combustion of an ammonia-hydrogen mixture  
84 under the homogeneous charge compression ignition (HCCI) mode in a 16:1 compression ratio engine. In their  
85 study, stable combustion was achieved with up to 70% ammonia by volume fraction. The introduction of  
86 exhaust gas recirculation (EGR) can reduce the NO<sub>x</sub> emissions but degrades the combustion efficiency due to  
87 the lower in-cylinder temperature.

88 Because of the poor solubility of liquid ammonia in gasoline and diesel, it is difficult to directly blend  
89 ammonia with gasoline or diesel. Therefore, when gasoline or diesel is used as the combustion promoter, the

90 dual-fuel strategy is usually adopted to implement ammonia combustion. Reiter and Kong [17] investigated  
91 the combustion and emission characteristics of a CI engine using a dual-fuel approach with PFI of ammonia  
92 and direct-injection (DI) of diesel. They found that the CO<sub>2</sub> and soot emissions were significantly decreased  
93 with the increased ammonia under the same torque output. When ammonia accounted for less than 40% of the  
94 total fuel energy, the NO<sub>x</sub> emission was also reduced because the lower flame temperature led to the decreased  
95 thermal NO<sub>x</sub>. Moreover, it is noted that the DI of gaseous ammonia in a SI engine has been attempted by Ryu  
96 et al. [24]. The PFI of gasoline was employed to initiate combustion and then gaseous ammonia was directly  
97 injected into the cylinder. They found that the overall brake-specific energy consumption using gasoline-  
98 ammonia is comparable to that using pure gasoline. Besides, the CO emission was observed to decrease,  
99 however, the NO<sub>x</sub> and HC emissions were increased. Gross and Kong [26] developed a high-pressure mixing  
100 tank to blend liquid ammonia with DME and investigated the combustion and emission characteristics in a CI  
101 engine. Their results showed that the addition of ammonia to DME leads to the lower combustion pressure and  
102 temperature, and therefore the higher CO and HC emissions. The NO<sub>x</sub> emission is also increased due to the  
103 formation of fuel NO<sub>x</sub>, which however can be improved by increasing the injection pressure.

104 From the above literature review, although the utilization of pure ammonia as a fuel in engines is very  
105 challenging, it is of great significance for the requirements of zero-carbon emission and control of global  
106 temperature rise. Compared with PFI method, the gaseous ammonia DI strategy seems to be the more  
107 promising way to achieve pure ammonia combustion in engines, however, the relevant studies are quite few.  
108 The premixed combustion in PFI might cause significant unburned ammonia due to its quite low laminar flame  
109 speed. The DI diffusion combustion could reduce the unburned ammonia and therefore decrease ammonia slip  
110 which can cause air pollution and hazard to health. In addition, the PFI of gaseous ammonia will displace a  
111 certain amount of air delivered to the combustion chamber, reducing the volumetric efficiency and therefore

112 the output power of engines, while the DI of gaseous ammonia has more potentials for maintaining the charging  
113 efficiency and engine power.

114 As a consequence, we aim at developing the pure-ammonia-fueled engines by the DI of gaseous ammonia  
115 into the cylinder, which has the potentials to decrease ammonia slip and increase the output power. To realize  
116 the DI of gaseous ammonia in engines, it is essential to make clear of the injection characteristics and the  
117 ammonia-air mixing process of ammonia jets. To the best of the present authors' knowledge, this is the first  
118 study on investigating the injection and mixing characteristics of gaseous ammonia jets. For this purpose, the  
119 ammonia jets were captured by a high-speed Schlieren imaging system to analyze the macroscopic  
120 characteristics including tip penetration and jet angle. Moreover, the fuel concentrations in ammonia jets were  
121 quantitatively measured by the laser-induced breakdown spectroscopy (LIBS) technique to study the ammonia-  
122 air mixing process.

123 The paper is structured as follows. The experimental systems including the Schlieren imaging and the  
124 LIBS measurement technique are firstly described. Then, the image processing and definitions of jet  
125 characteristics including tip penetration and jet angle are illustrated. After the time-resolved tip penetration is  
126 analyzed, the effects of injection pressure and ambient pressure on both tip penetration and jet angle are  
127 investigated. The pre-calibrations between the peak intensity ratio (PIR) and equivalence ratio ( $\phi$ ) are built up,  
128 followed by the detailed analysis on the shot-to-shot fluctuations of equivalence ratio in ammonia jets. Then,  
129 the effects of injection pressure and ambient pressure on fuel concentrations in ammonia jets are confirmed.  
130 During the above analysis, meanwhile, the characteristics of DI ammonia jets are also used to compare with  
131 those of methane jets. Finally, the major conclusions are summarized.

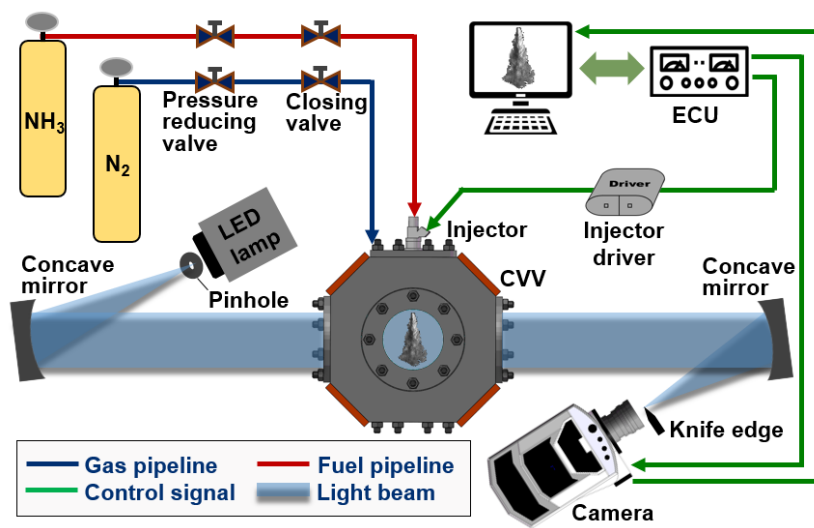
## 132 **2. Experimental apparatus and procedure**



133 2.1. Constant volume vessel and fuel injection

134 Figure 1 shows the schematic of the Schlieren imaging setup for gas jets. An optically-accessible constant  
135 volume vessel (CVV) was designed to visualize the gas injections under various ambient and injection  
136 conditions. The CVV provided three optical windows with 90-mm diameters [28]. A single-hole swirl injector  
137 with a hole diameter of 0.93 mm was installed on the top of the CVV. A gas cylinder was connected to the  
138 injector to supply the fuel gas. During the test, the air was firstly introduced into the CVV with the ambient  
139 pressure ( $P_a$ ) monitored by a piezo-resistive pressure sensor. Then, the fuel gas from the high-pressure gas  
140 cylinder was relieved to the targeted injection pressure ( $P_{inj}$ ) by a pressure regulator and then injected into the  
141 CVV in the gaseous state. After each injection, the CVV was fully purged by the fresh air. The measurements  
142 were performed at the room temperature of 298 K, and the saturated vapor pressure of ammonia is 10.0 bar.  
143 To avoid the liquefaction of ammonia gas, the injection pressures were varied from 4.0 to 8.0 bar. Although  
144 the employed injection pressures are relatively low, a previous study showed that the jet characteristics were  
145 mainly dependent on the pressure ratio (PR) rather than the absolute injection pressure [29]. The PR is defined  
146 as the ratio between the injection pressure and the ambient pressure, and it ranges from 2.0 to 8.0 in this study.  
147 When the PR is larger than the critical value (1.9 for ammonia calculated by  $(\frac{\gamma+1}{2})^{\frac{\gamma}{\gamma-1}}$ , considering the  
148 specific heat ratio as 1.313 for ammonia), the jet is choked and become underexpanded. The employed  
149 ambient pressures are lower than the cylinder pressure near the top dead center in DI gas engines. However,  
150 due to the low volumetric energy density of gaseous ammonia, a relatively long injection duration may be  
151 required to ensure that sufficient fuel is injected into the cylinder. The most importance is that, in some  
152 injection strategies in gas engines, the injection timing is quite advanced (approximately either near the TDC  
153 of intake process or the initial compression process) to ensure the enough mixing time because the mixing

154 process in gas jets is less efficient than that in liquid sprays. As a consequence, the cylinder pressure during  
 155 the injection period goes through a wide range of ambient pressures. The Reynolds number at the nozzle exit  
 156 is estimated by assuming the isentropic flow in the nozzle [30]. At the injection pressure of 8.0 bar and the  
 157 supply fuel temperature of 298 K, the Reynolds number at the nozzle exit for ammonia jets is about 130000.  
 158 The injection duration ( $\tau$ ) was set to 2.0 ms during all measurements. In addition to the ammonia, the injections  
 159 of methane were also conducted for comparisons. The experimental conditions are summarized in Table 1.



160  
 161 **Fig. 1.** Schematic of the Schlieren imaging setup for gas jets.

162 **Table 1** Experimental conditions

Fuel type	NH <sub>3</sub> (base), CH <sub>4</sub> (comparison)
Ambient temperature (K)	298
Ambient pressure (bar)	1.0-4.0
Injector hole diameter (mm)	0.93
Injection pressure (bar)	4.0-8.0
Injection duration (ms)	2.0
Room temperature (K)	298

163 *2.2. Schlieren imaging system*

164 The time evolutions of ammonia jets inside the CVV were recorded using a Z-type high-speed Schlieren  
 165 imaging technique. The Schlieren technique enables to detect the boundary between the gas jet and the ambient

166 gas due to the difference in refractive index, and therefore to investigate the macroscopic characteristics of gas  
167 jets. As shown in Fig. 1, the light from a light-emitting diode (LED) lamp was transformed into a point light  
168 source by a pinhole. Then, the light beam was collimated by a concave mirror with 500-mm focal length. The  
169 parallel light passed through gas jets in the CVV and transmitted the information of jet characteristics to the  
170 high-speed camera (Phantom V2012) through a concave mirror with 500-mm focal length and a knife-edge at  
171 the focus. Jet images were recorded at a speed of 50000 frames per second and a resolution of  $512 \times 256$  pixels.  
172 The frame exposure was set to  $5 \mu\text{s}$ . By using a 50-mm Nikon f/1.4 lens, the projected pixel size of the camera  
173 is 0.15 mm/pixel. The synchronization of injection and imaging was achieved by a programmable electronic  
174 control unit (ECU).

### 175 *2.3. Image processing and definitions of jet characteristics*

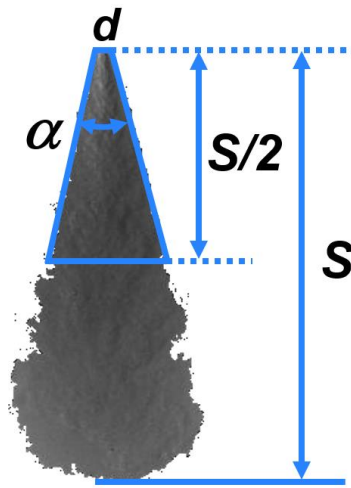
176 For the image processing of Schlieren images, the background images were firstly taken before the gas  
177 injections. After the fuel gas was injected, there were significant density gradients in the jets, causing variations  
178 of pixel intensity in the jet region. Then, the absolute values of the differences between the background images  
179 and the jet images were calculated. After a  $3 \times 3$  pixel median filtering was implemented to improve the signal-  
180 to-noise ratio (SNR), the Canny edge detection algorithm was employed to detect the jet boundary [31]. This  
181 algorithm is based on finding the local maximum of intensity gradient in the jet image, and it enables to  
182 distinguish unclear edges. The binary images obtained from the Canny algorithm were further processed by  
183 dilation and filling operations to identify the jet region. After the jet region was determined, the jet  
184 characteristics including tip penetration, jet angle, and jet volume were analyzed. Figure 2 depicts the  
185 definitions of tip penetration and jet angle of ammonia jets. The tip penetration ( $S$ ) is defined as the distance  
186 from the nozzle hole exit to the jet front edge. It should be noted that the jet has a certain width at the nozzle

187 exit, which cannot be ignored when determining the jet angle, especially for the first few jet images. Therefore,  
188 the jet angle ( $\alpha$ ) is evaluated by considering the upper half of the jet's projection area as an isosceles trapezoid  
189 instead of a triangle. Then the jet angle can be calculated by:

190 
$$\alpha = \frac{360}{\pi} \arctan \frac{4A - 2dS}{S^2} \quad (1)$$

191 where  $d$  is the nozzle hole diameter [mm] and  $A$  is the upper half of the jet's projection area [mm<sup>2</sup>] determined  
192 based on the binary image.

193



194

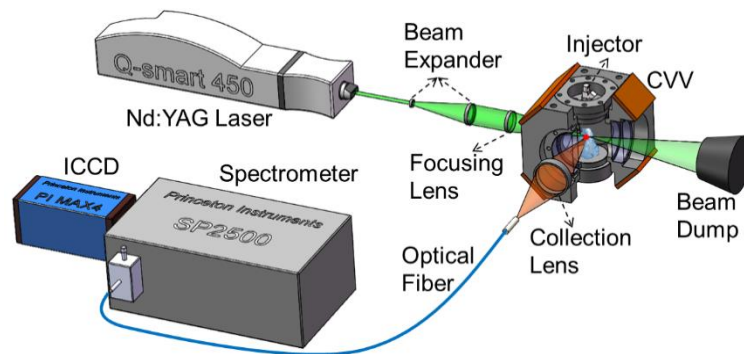
195 **Fig. 2.** Definitions of tip penetration and jet angle.

196 *2.4. LIBS concentration measurement system*

197 Fuel concentration information is crucial since it characterizes the fuel-air mixing and determines not  
198 only the ignition process but also the combustion process. In this study, the LIBS technique was employed to  
199 quantitatively measure the fuel concentrations in ammonia jets. The LIBS technique is an atomic emission  
200 spectroscopic technique. A high-energy laser pulse is tightly focused on the target and the resulting plasma  
201 emission is dispersed and analyzed. Compared with other laser-based techniques, the LIBS technique has

202 particular advantages, including the excellent SNR, high precision in quantification, independence on the  
203 molecules, and diversity of fuel forms such as solids, liquids, and gases.

204 The schematic of the LIBS measurement system is shown in Fig. 3. The laser beam with 6.5-mm diameter  
205 from a 532-nm Nd:YAG laser (Quantel Q-smart 450) was firstly expanded to 50 mm in diameter and then  
206 focused into the CVV using a 200-mm focal length plano-convex lens. The pulse energy ( $E$ ) before the  
207 focusing lens was about 137 mJ with a standard deviation of 2.9%. The plasma emission was collected by a  
208 100-mm focal length lenticular lens and then coupled into an optical bundle. The plasma signal was dispersed  
209 by a spectrometer (Princeton Instruments SP2500) with a 150-grooves/mm diffraction grating and finally  
210 imaged on an intensified charge-coupled device (ICCD) camera (Princeton Instruments PI MAX4). The delay  
211 and width of the ICCD gate were optimized to be 0.4 and 0.5  $\mu$ s respectively, according to the signal-to-  
212 background ratios (SBRs) of atomic lines and the stability of the PIR. The detailed information can be found  
213 in our previous study [32].

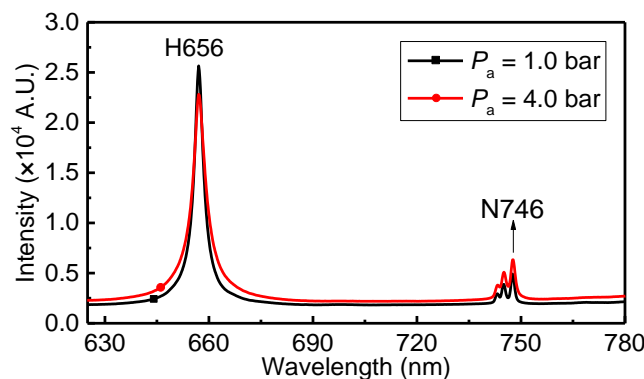


214  
215 **Fig. 3.** Schematic of the LIBS measurement system.

216 In the LIBS calibrations, the ammonia and the nitrogen as a substitute of the air from high-pressure gas  
217 bottles were sequentially transferred to the CVV to produce the homogeneous mixture of a certain equivalence  
218 ratio. The equivalence ratios of the mixture were estimated by assuming a 21% O<sub>2</sub> ambient and the partial  
219 pressure law. A motor-driven mixing fan was employed to enable the mixture as homogeneous as possible.

220 Then, the laser-induced breakdowns (LIB) were generated in the homogeneous mixture and the corresponding  
221 emission spectra were analyzed. For the LIBS measurements in ammonia jets, the CVV was firstly purged.  
222 After that, the nitrogen as the ambient gas was introduced into the CVV to the targeted pressure and then the  
223 gaseous ammonia was injected. At a certain time after the start of injection, the laser shot was emitted. After  
224 the emission spectrum was collected, the equivalence ratio can be determined by the peak intensity ratio (PIR).

225 Figure 4 shows the LIBS spectra of the ammonia-nitrogen mixture at the ambient pressures of 1.0 bar and  
226 4.0 bar. The equivalence ratio of the mixture is 0.95. The spectra are the average of 100 laser shots. It can be  
227 observed that the atomic lines of hydrogen and nitrogen dominate the emission spectra during the collection  
228 time of the ICCD. The hydrogen line at 656 nm, named H656 can be regarded as an indicator of ammonia gas.  
229 In addition, the strongest nitrogen line in N(I) band at 746.8 nm, termed N746 was employed to quantify the  
230 nitrogen atoms, which originate from both ammonia and ambient nitrogen. The peak intensity ratio (PIR) of  
231 H656 and N746 was employed to determine the equivalence ratio of the mixture. At the ambient pressure of  
232 4.0 bar, the baseline continuum emission is slightly increased as a result of the denser molecules and the  
233 intensified collisions. However, the line intensity of H656 remarkably reduces due to the stronger self-  
234 absorption effects at the higher gas pressure.

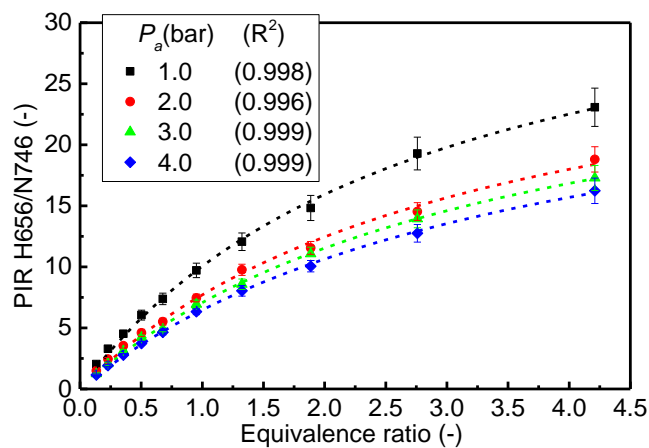


235  
236 **Fig. 4.** The LIBS spectra of ammonia-nitrogen mixture at the ambient pressures of 1.0 bar and 4.0 bar ( $T_a =$   
237 298 K,  $\phi = 0.95$ ,  $E = 137$  mJ).

238 2.5. Pre-calibrations of the LIBS measurement

239 To quantify fuel concentrations in the ammonia jets by LIBS, the pre-calibration is a necessity. The  
240 calibrations were performed by firstly producing a homogeneous ammonia-nitrogen mixture, achieving  
241 emission spectra from the laser-induced plasma in the mixture, and then constructing correlations between the  
242 intensity ratios of atomic lines and the concentration ratios of targeted atoms.

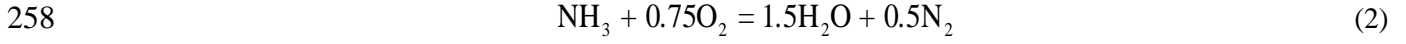
243 Figure 5 shows the LIBS calibration curves between the PIRs of H656/N746 and the equivalence ratios  
244 of ammonia-nitrogen mixture at different ambient pressures. Ten equivalence ratios ranging from 0.3 to 4.7  
245 were investigated, and a hundred tests were conducted at each equivalence ratio. The PIRs of H656/N746 are  
246 the averaged results and the error bars of PIRs represent the standard deviations for the average of a hundred  
247 shots. Generally, the PIRs increase with the equivalence ratio increasing at all ambient pressures. The  
248 correlations between PIRs and equivalence ratios show nonlinear behaviors because nitrogen atoms are from  
249 both the ambient nitrogen molecule and ammonia. It is also observed that the PIRs decrease with the increased  
250 ambient pressure. This is mainly attributed to the difference in the self-absorption effects on H656 and N746.  
251 The self-absorption effects for H656 line are more prominent than N746 line due to the higher transition  
252 probability. As the ambient gas pressure increases, the self-absorption is intensified, and therefore the line  
253 intensity of H656 reduces more significantly than that of N746 [33].



254

255 **Fig. 5.** The calibration curves between the PIRs of H656/N746 and the equivalence ratios of ammonia-  
256 nitrogen mixture at different ambient pressures ( $T_a = 298$  K,  $E = 137$  mJ).

257 The equivalence ratio of ammonia-nitrogen mixture is calculated by the following reaction:



259 When considering the pure nitrogen as the ambient air with 21% oxygen, the mole ratio of ammonia and  
260 nitrogen can be expressed as:

$$261 \quad n_{\text{NH}_3}/n_{\text{N}_2} = \frac{0.21}{0.75}\phi \quad (3)$$

262 where  $n_{\text{NH}_3}$  and  $n_{\text{N}_2}$  are the moles of ammonia molecule and nitrogen molecule (mol), respectively. Then, the  
263 mole ratio of atom hydrogen and atom nitrogen is given as:

$$264 \quad n_{\text{H}}/n_{\text{N}} = 3\phi / (\phi + 7.14) \quad (4)$$

265 where  $n_{\text{H}}$  and  $n_{\text{N}}$  are the moles of hydrogen and nitrogen atom (mol), respectively. It can be seen that the  
266 relation between the mole ratio of the hydrogen and nitrogen atom and the equivalence ratio shows a nonlinear  
267 behavior. Moreover, based on the principle of LIBS, the intensity ratio of two atomic lines is proportional to  
268 the concentration ratio of corresponding atoms. As a result, the correlations between the PIRs of H656/N746  
269 and the equivalence ratios of ammonia-nitrogen mixture can be fitted by the following equation:

$$270 \quad \text{PIR} = a\phi(\phi + b) \quad (5)$$

272 where  $a$  and  $b$  are constants. The dashed lines in Fig. 5 show the calculated results by Eq. (5). The  $R^2$  of  
273 calibration curves at different pressures are all over 0.99, i.e. the PIR of H656/N746 can accurately quantify  
274 the equivalence ratio of the ammonia-nitrogen mixture. In addition, the PIRs show a deviation of 3-7% from  
275 the mean value, indicating a high measurement precision. The total measurement uncertainties of LIBS



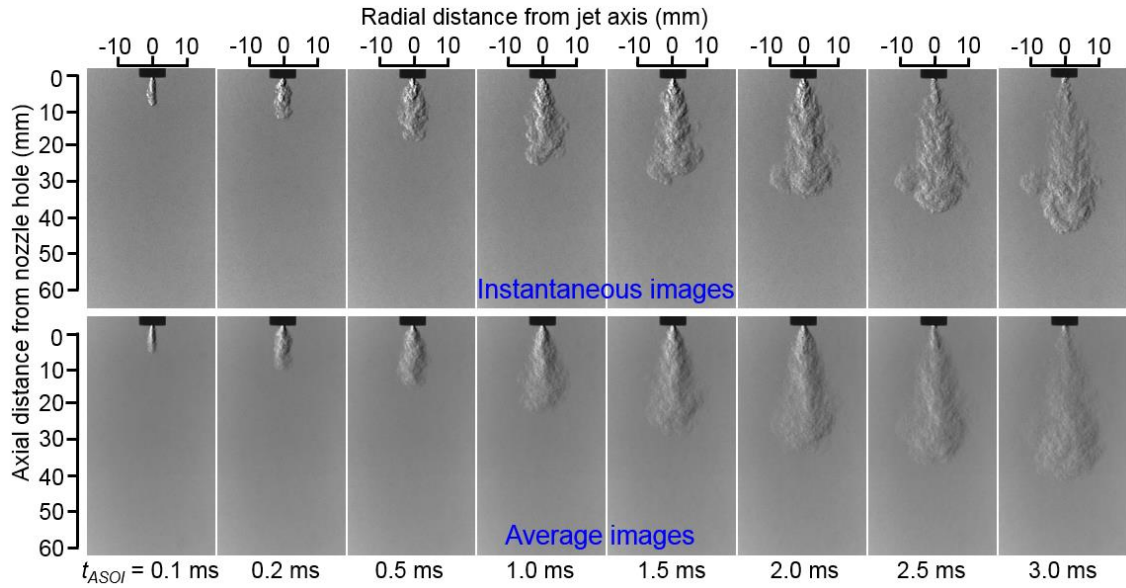
276 concentration measurements are estimated to be 5-10% by considering the inaccuracy in the equivalence ratio  
277 calibrations and the laser pulse instability [32].

### 278 **3. Results and discussion**

#### 279 *3.1. Jet characteristics by Schlieren image*

280 In this section, the Schlieren images of ammonia jets at different injection and ambient conditions are  
281 presented. The time dependence of jet characteristics is analyzed in detail, including tip penetration and jet  
282 angle which are influential factors on the fuel-air mixing process in DI engines.

283 Figure 6 shows the Schlieren images of ammonia jets at different time after the start of injection ( $t_{ASOI}$ ) at  
284 the injection pressure of 8.0 bar and the ambient pressure of 2.0 bar. The top and bottom rows are the  
285 instantaneous images and corresponding average images for five injections, respectively. As shown in Fig. 6,  
286 after the needle starts to lift, the ammonia gas comes out of the nozzle hole and the jet penetrates rapidly. At  
287  $t_{ASOI} = 0.1$  ms, the jet is relatively narrow, probably due to a tiny flow area of ammonia gas at the early stage  
288 of the needle lifting process. In the instantaneous images, the asymmetrical jet structures with high fluctuations  
289 are clearly observed. The jet edge and jet tip are significantly bent by strong turbulence. A stream of fuel gas  
290 is squeezed out of the jet at  $t_{ASOI} = 2.0$  ms. For the gas injection with the PR larger than the critical pressure  
291 ratio (1.84 for ammonia), the gas flow is choked in the nozzle hole, and therefore the complex shock structures  
292 are induced near the nozzle exit, making the jet highly turbulent. It was reported that the ambient air would be  
293 entrained into the gaps between the large-scale turbulent structures along the jet boundaries and jet tips,  
294 effectively promoting the fuel-air mixing during the end of injection (EOI) transients [34].



295

296 **Fig. 6.** Instantaneous and averaged Schlieren images of ammonia jets at different  $t_{ASOI}$  ( $P_{inj} = 8.0$  bar,  $P_a = 2.0$

297

bar,  $T_a = 298$  K,  $\tau = 2.0$  ms).

298

The jet tip penetration and jet angle are determined based on the Schlieren images and the image

299

processing procedures. Figure 7 depicts the time evolutions of averaged tip penetration and jet angle of

300

ammonia jets at the injection pressure of 8.0 bar and the ambient pressure of 2.0 bar. The error bars represent

301

the standard deviations for five injections. The time evolution of tip penetration shows an approximately linear

302

trend before  $t_{ASOI} = 0.1$  ms. After that, the tip penetration speed gradually decreases due to the momentum

303

exchange between the high-speed jet and the ambient gas. The time evolution of jet angle shows a transient

304

stage before  $t_{ASOI} = 0.4$  ms, during which the jet angle increases. This is consistent with the narrow jet at  $t_{ASOI}$

305

$= 0.1$  ms observed in Fig. 6. After  $t_{ASOI} = 0.4$  ms, the jet angle gradually decreases. In addition, relatively larger

306

fluctuations of jet angles can be observed after the EOI due to the weak Schlieren effects around the jet tail.

307

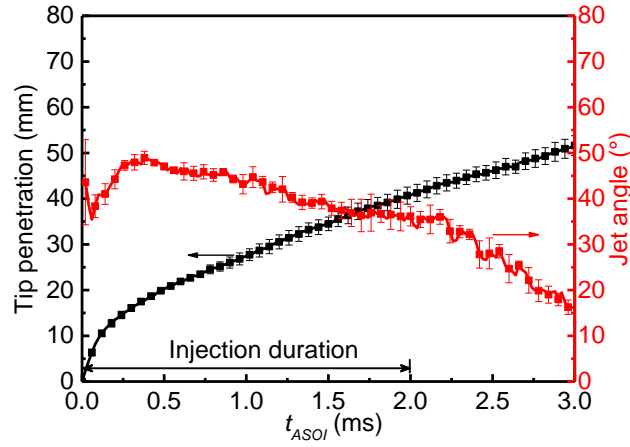
Although the instantaneous images of ammonia jets involve remarkable turbulence as shown in Fig. 6, the

308

error bars of both tip penetration and jet angle in Fig. 7 are quite small, indicating high repeatability of the

309

tests.



310

311 **Fig. 7.** Time evolutions of averaged tip penetration and jet angle of ammonia jets for five injections ( $P_{inj} =$

312

8.0 bar,  $P_a = 2.0$  bar,  $T_a = 298$  K,  $\tau = 2.0$  ms).

313

Figure 8 shows the time evolution of tip penetration at different stages. The injection and ambient

314

pressures are 8.0 bar and 2.0 bar, respectively. The logarithmic coordinates are used here to exhibit more

315

clearly the time dependence characteristics of tip penetration. In general, a three-stage behavior of jet tip

316

penetration can be significantly observed. Stage 1 is from the start of injection to about  $t_{ASOI} = 0.7$  ms. During

317

the Stage 1, the tip penetration firstly exhibits a  $t$  dependence before approximately  $t_{ASOI} = 0.1$  ms, and then

318

the slope of the curve decreases gradually. The linear behavior of the time evolution of tip penetration at the

319

beginning of injection for gas jets has also been observed by Gerold et al. [35]. Moreover, the tip penetrations

320

of diesel sprays also exhibit a  $t$  dependence before the spray break-up time [36] as below:

321

$$S = K_v (2\Delta P / \rho_a)^{0.5} t_{ASOI} \quad (6)$$

322

where  $K_v$  is the model constant,  $\Delta P$  indicates the pressure difference between the injection pressure and

323

ambient pressure, [Mpa],  $\rho_f$  is the fuel density, [ $\text{kg}/\text{m}^3$ ], and  $t_{ASOI}$  is the time after the start of injection, [ms].

324

The diesel sprays do not break up completely before the spray break-up time. Consequently, the momentum

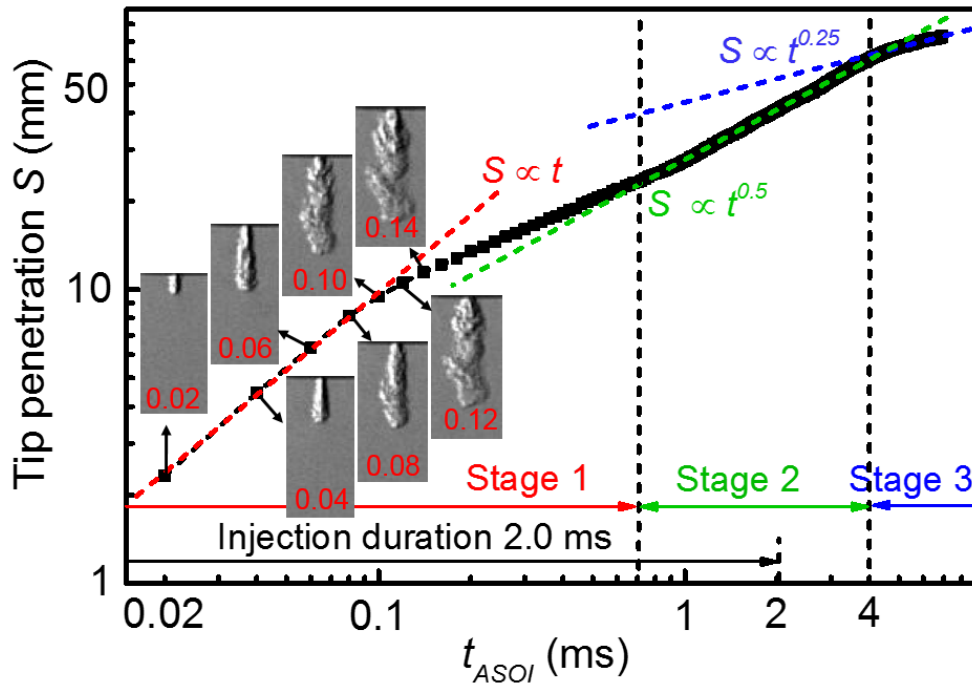
325

decay of the spray tip caused by the air resistance is relatively small, leading to a nearly constant-speed

326

penetration during this period. However, the gas jets involve no break-up process. Therefore the fundamental

327 mechanism of the linear behavior of tip penetration in gas jets at the beginning of injection is different from  
 328 that in liquid sprays.



329  
 330 **Fig. 8.** Three-stage behavior of the tip penetration of ammonia jets. ( $P_{inj} = 8.0$  bar,  $P_a = 2.0$  bar,  $T_a = 298$  K,  $\tau$   
 331  $= 2.0$  ms).

332 Some studies showed that the behavior of tip penetration during the initial injection is strongly related to  
 333 the needle valve movement [37, 38]. At the beginning of the injection, the needle lift is quite small, causing a  
 334 meager mass flow rate, and the gas flow has not been choked in the nozzle hole during this period. Therefore  
 335 the jet involves little shock-induced turbulence. The shock-induced turbulence is also called the Richtmyer–  
 336 Meshkov instability. It is induced by a shock wave colliding with an interface between two fluids of different  
 337 density. When two kinds of fluids are impulsively accelerated into each other by the shock wave, small  
 338 perturbations at the interface gradually evolve into non-linear structures formed of “bubbles” and “spikes”.  
 339 Then, it may lead to the formation of a turbulent mixing zone. The shock-induced turbulence may strongly  
 340 affect the flow structure and turbulent mixing [39, 40]. As shown in Fig. 8, the jet boundary is smooth before

341  $t_{ASOI} = 0.1$  ms, but after that it is remarkably disturbed. Lei et al. reported that at the beginning of injection, the  
342 turbulence kinetic energy is relatively low both inside and outside the nozzle and then significantly increases  
343 after few hundreds of microseconds [41]. As a result of very weak shock-induced turbulence, the ambient air  
344 entrainment into the gas jet is dominated by the shear-induced turbulence. Therefore, the momentum exchange  
345 between the high-speed jet and ambient air would be small, causing nearly uniform jet tip penetration. This  
346 turning point at the end of uniform penetration is named the undisturbed endpoint. After the undisturbed  
347 endpoint, the curve slope gradually decreases, indicating that the jet experiences a deceleration process. This  
348 is due to the enhanced shock-induced turbulence in gas jets, as shown by the jet images after  $t_{ASOI} = 0.1$  ms in  
349 Fig. 8. It should be noted that the behavior of tip penetration at the beginning of injection largely depends on  
350 the inner structure of the injector nozzle and therefore can be distinct by using different types of injector. In  
351 the studies of Erfan et al. [31] and Dong et al. [42], the tip penetration shows a  $t^{0.5}$  dependence at the near  
352 nozzle region, but the slope of  $S-t^{0.5}$  curve is different from that at the far nozzle region.

353 From about  $t_{ASOI} = 0.7$  ms, the jet goes into the quasi-steady state, which is the main period of jet  
354 development. During this stage, the tip penetration correlates well with  $t^{0.5}$ . Ouellette and Hill [43] developed  
355 a model to evaluate the tip penetration of gas jets based on the experimental data and the momentum  
356 conservation principle, as shown in Eq. (7):

$$357 \quad S = \Gamma (\dot{M}_n^g / \rho_a)^{0.25} \sqrt{t_{ASOI}} \quad (7)$$

$$358 \quad \dot{M}_n^g = c_d A_n \rho_n U_n^2 \quad (8)$$

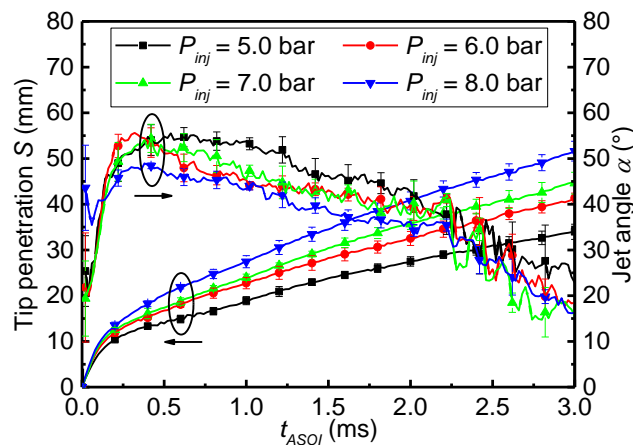
359 where  $S$  is the tip penetration [mm],  $\Gamma$  is the penetration constant [-],  $\dot{M}_n$  is the momentum injection rate  
360 [kg·m/s<sup>2</sup>] which can be expressed by Eq. (8).  $U_n$  is the choked velocity in nozzle hole [m/s].  $A_n$  is the cross-  
361 sectional area of nozzle hole [mm<sup>2</sup>].  $c_d$  is the discharge coefficient [-] and  $\rho_n$  is the density of fuel gas at the  
362 nozzle hole exit [kg/mm<sup>3</sup>]. The momentum injection rate is nearly constant during the quasi-steady state. As a

363 result, the tip penetration has a  $t^{0.5}$  dependence. The jet tip decelerates due to significant entrainment of the  
364 ambient air produced by both shear-induced turbulence and shock-induced turbulence. Although the gas  
365 injection stops at  $t_{ASOI} = 2.0$  ms, the tip penetration behavior after the EOI still keeps consistent with the earlier  
366 time until about two times of injection duration. The time dependence of tip penetration during the quasi-  
367 steady state at various injection and ambient pressures for different fuel gases will be discussed in detail in the  
368 following.

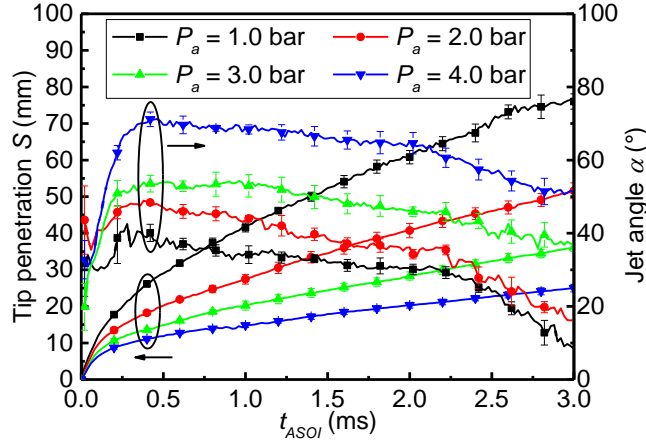
369 It can be observed that another turning point appears at about two times of injection duration. After this  
370 turning point, the tip penetration speed decreases more significantly. The behavior of tip penetration exhibits  
371 a  $t^{0.25}$  dependence until the end of camera recording. The available camera recording time mainly varies with  
372 the ambient pressure due to more significant Schlieren effects at the higher ambient pressures (e.g.  
373 approximately 7.0 ms at  $P_a = 2.0$  bar). The transitions of tip penetration from a square-root dependence on  
374 time to a fourth-root dependence at two times of injection duration have also been observed in diesel sprays  
375 by some researchers [44, 45], but rarely reported in gas jets. This phenomenon can be explained by the  
376 entrainment wave theory [46]. After the EOI, the deceleration state of diesel jet would travel from the nozzle  
377 to the jet tip with increased entrainment rate. After the front of entrainment wave arrives at the jet tip, the  
378 whole diesel jet goes into the deceleration state. As a consequence, the jet tip penetration gradually correlates  
379 with the fourth-root of time.

380 The effects of injection pressure and ambient pressure on tip penetration and jet angle of ammonia jets  
381 are shown in Figs. 9 and 10, respectively. The tip penetrations and jet angles are the averaged values, and the  
382 error bars stand for the standard deviations for five tests. As shown in Fig. 9, the time evolutions of tip  
383 penetration at different injection pressures keep consistent trends. The tip penetration is increased with the  
384 injection pressure increasing. As the injection pressure rises from 5.0 bar to 8.0 bar, the tip penetration at  $t_{ASOI}$

385 = 3.0 ms increases from 33 mm to 52 mm. This can be attributed to the larger gas density at the higher injection  
386 pressure, and therefore the increased momentum flow rate of ammonia gas in the nozzle hole. The jet angle  
387 and injection pressure are generally negatively correlated, but this correlation is very weak. At the higher  
388 injection pressure, the jets are more likely to develop toward the jet axial direction and contract at the radial  
389 direction, causing a lower jet angle. In Fig. 10, it can be seen that the ambient pressure shows more significant  
390 effects on the tip penetration and jet angle compared to the injection pressure as shown in Fig. 9. With an  
391 increase in the ambient pressure, the tip penetration reduces while the jet angle increases. At  $t_{ASOI} = 3.0$ ms, the  
392 tip penetration decreases from nearly 76 mm at 1.0 bar to about 24 mm at 4.0 bar. The effects of ambient  
393 pressure can be attributed to two aspects. On one hand, the higher ambient pressure will cause the lower  
394 pressure ratio, leading to the lower momentum of fuel gas. On the other hand, the ambient pressure also affects  
395 ambient density, which has a major role on the entrainment effects. At the higher ambient density, the  
396 resistance from ambient gas is increased, therefore, the ammonia jets tend to develop toward the radial  
397 direction.



398  
399 **Fig. 9.** The effects of injection pressure on tip penetration and jet angle of ammonia jets ( $P_a = 2.0$  bar,  $T_a =$   
400 298 K,  $\tau = 2.0$  ms).



401

402

**Fig. 10.** The effects of ambient pressure on tip penetration and jet angle of ammonia jets ( $P_{inj} = 8.0$  bar,  $T_a =$

403

298 K,  $\tau = 2.0$  ms).

404

Figures 11(a) and (b) show the fits of (a) tip penetrations  $S$  and (b)  $S/(\rho_n/\rho_a)^{0.25}$  with the square root of

405

$t_{ASOI}$  at different PRs. The dots in Fig. 11(a) are the raw data, and the dashed lines are the fitted curves of linear

406

correlations between tip penetration and the square root of  $t_{ASOI}$ . Here, the results before  $t_{ASOI} = 4.0$  ms are

407

employed since the time dependence of tip penetration changes after  $t_{ASOI} = 4.0$  ms. Generally, the tip

408

penetrations show linear correlations with the square root of time at different PRs. All coefficients of

409

determination ( $R^2$ ) are over 0.99. Significant deviations of experimental data with the fitted curves are observed

410

at the early stage of injection, which is consistent with the analysis in Fig. 8. It is found that the duration of

411

this deviation greatly depends on the ambient pressure, probably owing to the effects of ambient pressure on

412

the needle lift-off process. In addition, it can be seen that the slope of the fitted curve increases with the

413

increased PR. At the PR of 2.0, the tip penetrations are quite close despite the different injection and ambient

414

pressures. Ouellette and Hill [43] established an empirical formula for the tip penetration and time scales in

415

underexpanded flow. The jet tip penetration is considered as a function of the gas density at the nozzle exit

416

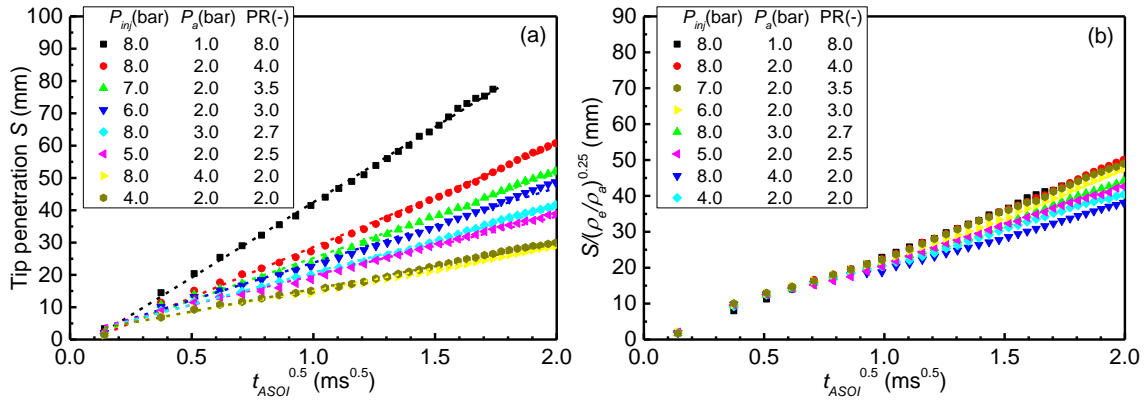
( $\rho_n$ ), ambient gas density ( $\rho_a$ ) and time after the start of injection ( $t_{ASOI}$ ) as:

417

$$S / (\rho_n / \rho_a)^{0.25} \propto t_{ASOI}^{0.5} \quad (9)$$



418 As shown in Fig. 11(b), the results at different PRs generally present similar evolution law. Slight deviations  
 419 can be observed at the low PRs since the flows are close to the subsonic condition at the PR of 2.0.



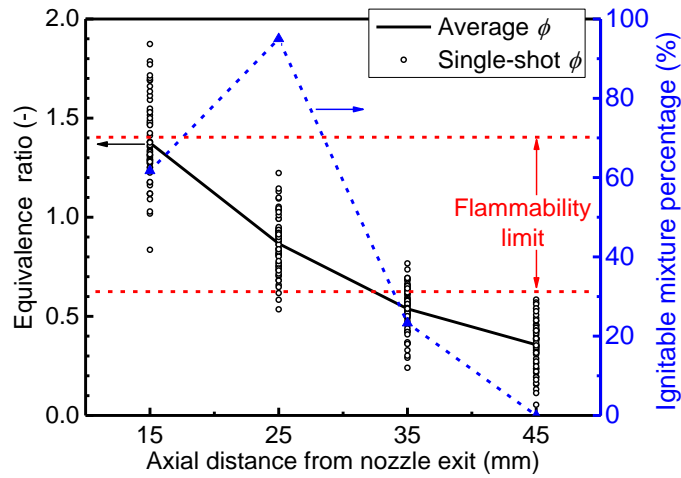
420

421 **Fig. 11.** Fits of (a) tip penetrations  $S$  and (b)  $S/(\rho_n/\rho_a)^{0.25}$  with the square root of  $t_{ASOI}$  at different PRs ( $T_a =$   
 422  $298\text{ K}$ ,  $\tau = 2.0\text{ ms}$ ).

423 *3.2. Fuel concentrations of ammonia jets*

424 Figure 12 shows the single-shot and the averaged equivalence ratios and the flammable mixture  
 425 percentage at different axial positions in ammonia jets. Each black circle indicates an equivalence ratio  
 426 obtained by a single laser shot. The averaged results of 60 times laser shots are marked by the black solid line.  
 427 The flammable mixture percentage is defined as the times in which the measured equivalence ratio is within  
 428 the flammability limit divided by the total measured times (60), and it is indicated by the blue dashed line. The  
 429 flammability limit for ammonia represented by the red dashed line is considered to be 0.63-1.40 at the pressure  
 430 of 1.0 bar and temperature of 298 K [2]. It is observed that the averaged equivalence ratio reduces with the  
 431 increased axial distance from nozzle exit due to the sufficient fuel-air mixing, and the decrease rate of  
 432 equivalence ratio becomes slow. The single-shot equivalence ratios at each axial position distribute in a wide  
 433 range, indicating the remarkable fluctuations of fuel concentration in ammonia jets. This is consistent with the  
 434 previous results in which significant shot-to-shot fluctuations of fuel concentration in natural gas jets were

435 observed [28, 47]. Generally, the gas jets would involve greater shot-to-shot variations than the liquid sprays  
 436 due to the instability in the gas expansion process and the inefficient fuel-air mixing [48].

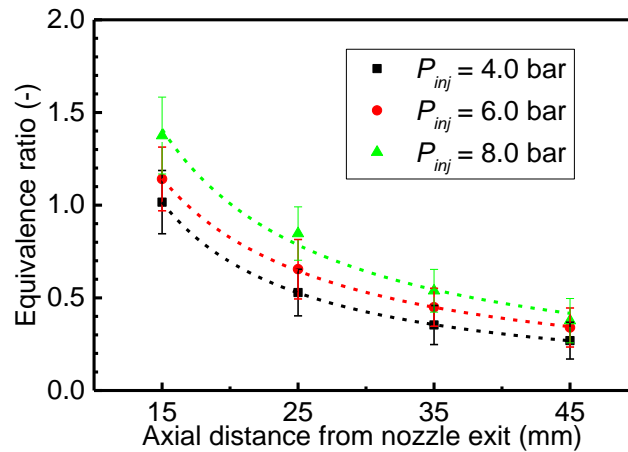


437  
 438 **Fig. 12.** The single-shot and the averaged equivalence ratios and the ignitable mixture percentage at different  
 439 axial positions in ammonia jets ( $P_{inj} = 8.0$  bar,  $P_a = 1.0$  bar,  $t_{ASOI} = 2.0$  ms,  $\tau = 2.0$  ms).

440 At 15 mm from the nozzle exit, the single-shot equivalence ratios widely distribute between 0.8 and 1.9  
 441 with an average of about 1.4, and 62% of the mixture is flammable. With the axial distance increasing, the  
 442 flammable mixture percentage firstly increases and then gradually reduces to zero. At 25 mm from nozzle exit,  
 443 the averaged equivalence ratio is 0.9 and up to 95% of the mixture is flammable, indicating a potentially  
 444 optimal ignition position within the four measuring positions. When the axial distance increases to 35 mm, the  
 445 averaged equivalence ratio is below the lower flammability limit, although the mixture is flammable in some  
 446 laser shots. The mixture becomes totally non-flammable at 45 mm from the nozzle exit.

447 Figure 13 shows the axial distributions of equivalence ratio in ammonia jets at different injection pressures.  
 448 The equivalence ratios are the averaged results, and the error bars represent the standard deviations for 60 tests.  
 449 It is reported that the axial variations of flow variables (e.g., fuel concentration and temperature) in the far-  
 450 field follow the hyperbolic decay [49, 50]. As a result, the axial distributions of equivalence ratio are fitted by  
 451 the hyperbolic curves, as shown in Fig. 13 by the dashed lines. The  $R^2$  of the fitted curves at different injection

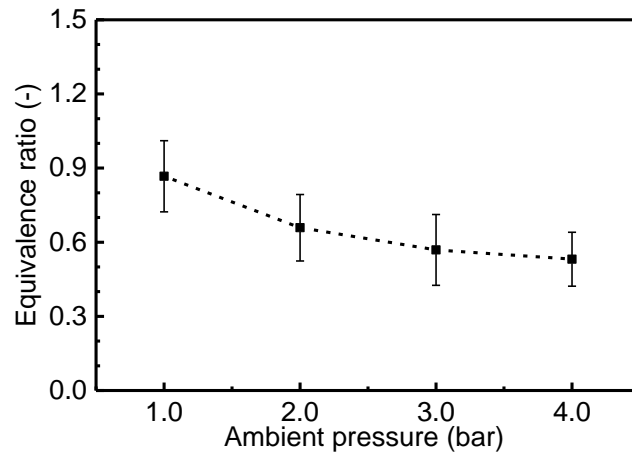
452 pressures are larger than 0.98, confirming the hyperbolic decay of fuel concentration along the jet centerline.  
 453 It can be seen that the equivalence ratios increase with the increased injection pressure at all four measuring  
 454 positions. In addition, there is no significant difference in fluctuations of equivalence ratio among the three  
 455 injection pressures. For the under-expanded gas jets, the flow in the injector hole is considered to reach its  
 456 critical conditions, i.e., the sonic speed and the critical pressure ratio in the throat of injector nozzle. As a result,  
 457 the mass flow rate of fuel gas in the nozzle hole proportionally increases with the injection pressure. Although  
 458 the air entrainment is stronger at the higher injection pressure, the mass flow rate increases more quickly,  
 459 leading to the larger equivalence ratios at the higher injection pressure.



460  
 461 **Fig. 13.** The axial distributions of equivalence ratio in ammonia jets at different injection pressures ( $P_a = 1.0$   
 462 bar,  $t_{ASOI} = 2.0$  ms).

463 Figure 14 depicts the effects of ambient pressure on the equivalence ratio in ammonia jets. The injection  
 464 pressure was kept at 8.0 bar, and the measuring position is 25 mm below the nozzle exit. The standard  
 465 deviations of the equivalence ratio indicated by the error bars are approximately 20% of the mean value at  
 466 different ambient pressures. Generally, the equivalence ratios gradually reduce with the increased ambient  
 467 pressure, and the decrease rate becomes slower. At the ambient pressure of 1 bar, the averaged equivalence  
 468 ratio falls within the flammable limit. The mixture at  $P_a = 2.0$  bar is over-lean, indicating more NO emission

469 would yield during combustion. When the ambient pressure is higher than 2.0 bar, the mixture turns to be non-  
 470 flammable. Since the flow is choked in the injector hole, the mass flow rate of fuel gas is mainly dependent  
 471 on the upstream pressure. Although the mass flow rate is not entirely independent of the ambient pressure, it  
 472 does not change considerably at different ambient pressures [31]. Therefore, when the injection pressure is  
 473 constant, the mass flow rate of fuel gas is considered to be very close at different ambient pressures. Moreover,  
 474 the air entrainment into the ammonia jet significantly increases at the higher ambient pressure due to both the  
 475 higher air density and the larger jet angle. Consequently, the fuel concentrations are decreased at the higher  
 476 ambient pressure.

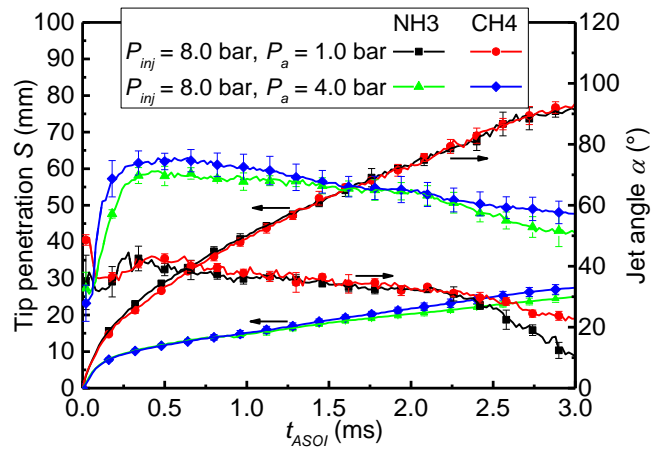


477  
 478 **Fig. 14.** The effects of ambient pressure on the equivalence ratio in ammonia jets at the injection pressure of  
 479 8.0 bar ( $z = 25$  mm,  $P_{inj} = 8.0$  bar,  $t_{ASOI} = 2.0$  ms).

### 480 3.3. Comparisons of ammonia and methane jets

481 Figure 15 shows comparisons of the tip penetration and jet angle between ammonia and methane jets.  
 482 The error bars in Fig. 15 represent the standard deviations for the average of five tests. The injection pressure  
 483 was kept at 8.0 bar, and two ambient pressures of 1.0 bar and 4.0 bar (PR = 2.0 and 8.0) were investigated.  
 484 Generally, Fig. 15 shows that the time evolutions of tip penetration in ammonia jets are pretty similar to those  
 485 in methane jets at the ambient pressures of both 1.0 bar and 4.0 bar. As shown in Eqs. (6) and (7), the tip

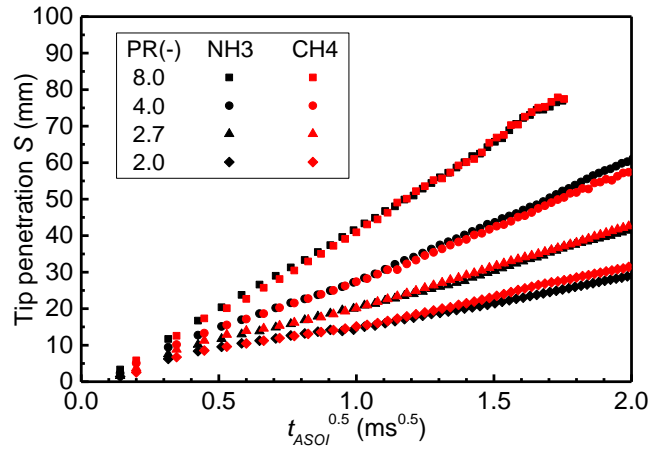
486 penetration is proportional to the fourth root of the fuel gas density. The gas density is proportional to the gas  
 487 molar mass at the constant gas pressure and temperature according to the ideal gas equation. Since the molar  
 488 mass of ammonia (17 g/mol) is very close to that of methane (16 g/mol), their tip penetrations are nearly  
 489 equivalent. At  $P_a = 1.0$  bar, the tip penetrations, and the jet angles between ammonia and methane jets are  
 490 nearly equal at different  $t_{ASOI}$ . Their jet angles gradually decrease as the jets develop. At the  $P_a = 4.0$  bar, the  
 491 time evolutions of tip penetrations and the jet angles between ammonia and methane jets are still consistent  
 492 during the injection. Only slight separation occurs after the EOI, which could be attributed to the slight  
 493 difference in molar mass between ammonia and methane. Generally, the time evolutions of ammonia and  
 494 methane jet characteristics, in terms of both tip penetration and jet angle, are quite similar. Consequently,  
 495 methane could be employed as a substitute for ammonia to study the macroscopic characteristic of ammonia  
 496 jets, especially for the under-expanded flow with the high PRs. This is critical since ammonia is very corrosive,  
 497 and thus the ammonia experiments would encounter significant challenges.



498  
 499 **Fig. 15.** Comparisons of tip penetration and jet angle between ammonia and methane jets at different  
 500 ambient pressures ( $P_{inj} = 8.0$  bar,  $T_a = 298$  K,  $\tau = 2.0$  ms).

501 The comparisons of tip penetration as a function of the square root of  $t_{ASOI}$  between ammonia and methane  
 502 jets at different PRs are depicted in Fig. 16. Four PRs from 2.0 to 8.0 were investigated. The black and red

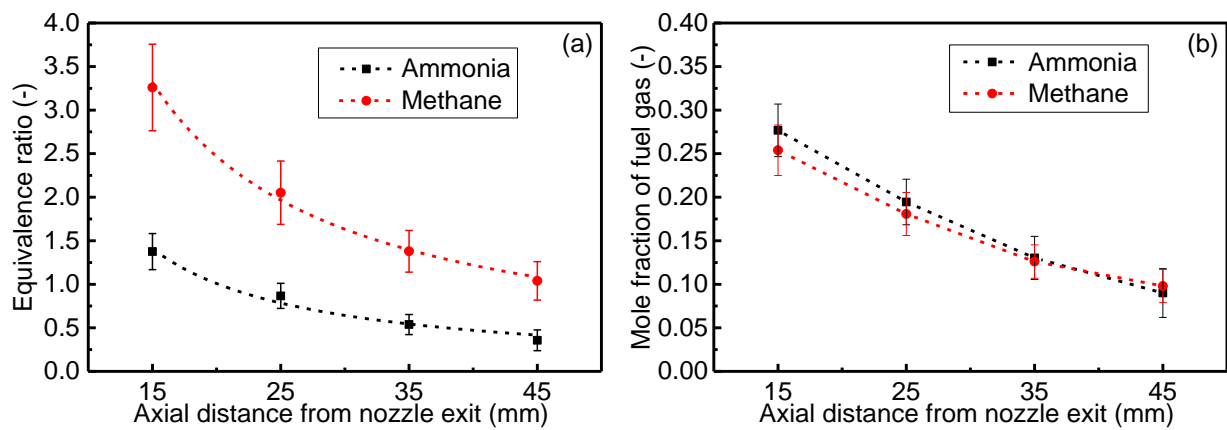
503 dots represent the results of ammonia and methane, respectively. Tip penetrations of both ammonia and  
 504 methane jets at different PRs linearly increase with the square root of  $t_{ASOI}$  increasing. Despite slight differences  
 505 at the late stage of jet development, the tip penetrations of ammonia and methane jets are almost equivalent.



506  
 507 **Fig. 16.** Comparisons of time evolutions of tip penetration between ammonia and methane jets at different  
 508 PRs ( $T_a = 298$  K,  $\tau = 2.0$  ms).

509 The comparisons of axial equivalence ratio distributions, and fuel mole fractions between ammonia and  
 510 methane jets are depicted in Figs. 17 (a) and (b), respectively. The injection and ambient pressures are 8.0 bar  
 511 and 1.0 bar, respectively. In Fig. 17 (a), the solid dots are the averaged equivalence ratios for 60 tests, and the  
 512 dashed lines represent the hyperbolic curve fits. It can be seen that the axial distributions of equivalence ratio  
 513 in both ammonia and methane jets fall well within the hyperbolic decay. Apparently, the equivalence ratios in  
 514 methane jets are significantly higher than those in ammonia jets. Although the error bars of equivalence ratio  
 515 in methane jets are wider than those in ammonia jets, the relative standard deviations (standard deviations for  
 516 the single tests divided by the mean values) are similar for ammonia and methane jets. The flammability limit  
 517 for methane is considered to be 0.5-1.7 at the pressure of 1.0 bar and temperature of 298 K [2]. For the methane  
 518 jets, the equivalence ratios at 15 mm and 25 mm below the nozzle exit are beyond the flammability limit. The  
 519 methane-air mixture is flammable downstream of 30 mm below the nozzle exit. In addition, the equivalence

520 ratio at 45 mm below the nozzle exit is around 1.1, in favor of a faster flame propagation if the mixture is  
 521 ignited here. However, the equivalence ratios in ammonia jets are significantly lower than those in methane  
 522 jets. From the perspective of fuel concentration, the flammable mixture distributions in methane jets are quite  
 523 different from those in ammonia jets. However, when the equivalence ratios are converted to the mole fractions  
 524 of fuel gas, the axial distribution of fuel mole fraction in ammonia jets is very close to that in methane jets, as  
 525 shown in Fig. 17 (b). At the stoichiometric conditions, one mole of ammonia consumes three quarters of a  
 526 mole of oxygen molecule, while one mole of methane consumes two moles of oxygen molecule. As a  
 527 consequence, for the same mole fraction of fuel gas, the equivalence ratio of methane-air mixture is 2.7 times  
 528 that of ammonia-air mixture, leading to the distinct flammable mixture distributions in ammonia and methane  
 529 jets. These results are very critical for researchers and engineers in calibrating numerical models and  
 530 determining the proper ignition and diffusion combustion for DI ammonia jets.



531  
 532 **Fig. 17.** The comparisons of axial distributions of (a) equivalence ratio and (b) fuel mole fraction between  
 533 ammonia and methane jets ( $P_{inj} = 8.0$  bar,  $P_a = 1.0$  bar,  $t_{ASOI} = 2.0$  ms).

534 Fuel-air mixing efficiency in gas jets is mainly controlled by the large-scale turbulent motion induced by  
 535 the shock and shear force and the small-scale motion for molecular mixing in the jet. In general, the large-scale  
 536 turbulent motion not only entrains surrounding air into the jet, but also gives turbulent energy for the jet, which  
 537 is necessary for molecular mixing with small-scale motion in the subsequent mixing process. The Reynolds

538 number at the nozzle exit in the ammonia jet under the injection pressure of 8.0 bar ( $\approx 130000$ ) is close to that  
539 in the methane jet ( $\approx 120000$ ), showing the similar turbulence intensity. Homogeneous mixture formation is  
540 mainly dependent on the molecular mixing in the small-scale motion. The diffusion coefficient between the  
541 fuel gas and air is a critical parameter in the molecular mixing process. Since the diffusion coefficient of  
542 ammonia in air ( $0.1978 \text{ cm}^2/\text{s}$  at 273 K and 1.0 bar) is similar to that of methane in air ( $0.1952 \text{ cm}^2/\text{s}$  at 273 K  
543 and 1.0 bar), their molecular mixing process is expected to be similar.

#### 544 **4. Conclusions**

545 The macroscopic characteristics of ammonia jets including tip penetration and jet angle have been  
546 investigated by using a high-speed Schlieren imaging system. Moreover, the fuel concentrations in ammonia  
547 jets have been quantitatively measured by the LIBS technique to study the ammonia-air mixing process. Tests  
548 in methane jets have been also conducted for the comparisons. The major conclusions are summarized as  
549 follows:

- 550 • The time evolution of tip penetration shows a three-stage behavior. The tip penetration exhibits a  $t$ ,  $t^{0.5}$  and  
551  $(t - \tau)^{0.25}$  dependence corresponding to the very early stage of injection, the quasi-steady stage and after two  
552 times of injection duration, respectively.
- 553 • The tip penetration shows a  $t$  dependence at the very early injection stage, which might be attributed to the  
554 jets involving little shock-induced turbulence and, therefore, having few momentum exchanges with the  
555 ambient gas.
- 556 • During the quasi-steady state, the jet tip penetration is linearly correlated with the square root of  $t$  under  
557 different PRs. Besides, the jet tip penetration greatly depends on the pressure ratio.



- 558 • In general, the time evolutions of tip penetration and jet angle for ammonia and methane jets are quite  
559 similar due to the close molar mass. Consequently, methane can be employed as a substitute of ammonia  
560 to study the macroscopic characteristic of ammonia jets.
- 561 • The hyperbolic decays of fuel concentrations at the jet axis in both ammonia and methane jets are  
562 confirmed experimentally.
- 563 • The fuel concentrations in ammonia jets increase with the increased injection pressure due to the larger  
564 mass flow rate of fuel gas. However, they significantly reduce with the increased ambient pressure because  
565 of the higher air density.
- 566 • The axial distributions of fuel mole fraction are nearly equivalent in ammonia and methane jets at the same  
567 injection and ambient conditions. However, the equivalence ratios in methane jets are significantly higher  
568 than those in ammonia jets, leading to the distinct flammable mixture distributions in ammonia and  
569 methane jets.

## 570 **Acknowledgments**

571 The financial supports by the National Natural Science Foundation of China (51776125) and the Major  
572 International (Regional) Joint Research Project of National Natural Science Foundation of China  
573 (52020105009) are gratefully acknowledged. The contributions by the graduate students in the Large Engine  
574 Research Center of NAOCE in SJTU are highly appreciated.

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677 **Nomenclature**

- 678  $A$  the area of upper half of the jet's projection ( $\text{mm}^2$ )
- 679  $A_n$  the area of nozzle hole ( $\text{m}^2$ )
- 680 ASOI after the start of injection
- 681  $c_d$  discharge coefficient (-)
- 682 CI compression-ignition
- 683 COP21 Conference of Parties 21

684	CVV	constant volume vessel
685	$d$	the nozzle hole diameter (mm)
686	DME	dimethyl ether
687	DI	direct injection
688	$E$	laser pulse energy (mJ)
689	EGR	exhaust gas recirculation
690	EOI	end of injection
691	ECU	electronic control unit
692	fps	frames per second
693	FWHM	full width at half maximum (nm)
694	FAR	fuel-air ratio (-)
695	HCCI	homogeneous charge compression ignition
696	ICCD	intensified charge coupled device
697	ICE	internal combustion engine
698	$K_v$	model constant
699	LED	light emitting diode
700	LIB	laser-induced breakdown
701	LIBS	laser-induced breakdown spectroscopy
702	$\dot{M}_n$	momentum injection rate ( $\text{kg}\cdot\text{m}/\text{s}^2$ )
703	$n_H$	the mole of hydrogen atom (mol)
704	$n_N$	the mole of nitrogen atom (mol)
705	$n_{NH3}$	the mole of ammonia molecule (mol)

706	$n_{N_2}$	the mole of nitrogen molecule (mol)
707	$P_a$	ambient pressure (bar)
708	$P_{inj}$	injection pressure (bar)
709	PIR	peak intensity ratio (-)
710	PR	pressure ratio (-)
711	$R^2$	coefficients of determination (-)
712	$S$	tip penetration (mm)
713	SBR	signal-to-background ratio (-)
714	SCR	selective catalytic reduction
715	SNR	signal-to-noise ratio (-)
716	SI	spark-ignition
717	$t_{ASOI}$	time after the start of injection (ms)
718	$t_a$	ambient temperature (K)
719	$U_n$	the choked velocity in nozzle hole (m/s)
720	$\alpha$	jet angle ( $^\circ$ )
721	$\tau$	injection duration (ms)
722	$\phi$	equivalence ratio (-)
723	$\Gamma$	penetration constant (-)
724	$\rho_f$	fuel density (kg/m <sup>3</sup> )
725	$\rho_n$	the density of fuel gas at the nozzle hole exit (kg/m <sup>3</sup> )
726	$\Delta P$	pressure difference between the injection pressure and ambient pressure (bar)