

1                   **Towards Carbon-Free Mobility: The Feasibility of**  
2                   **Hydrogen and Ammonia as Zero Carbon Fuels in Spark Ignition**  
3                   **Light-Duty Vehicles**

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18 **Abstract**

19 Global warming is a major environmental issue caused by the release of greenhouse gases,  
20 such as carbon dioxide into the atmosphere. Light-duty vehicles (LDVs) including passenger  
21 cars and light-duty trucks, are a significant contributor to greenhouse gas emissions. The  
22 transportation sector is responsible for approximately 23% of global CO<sub>2</sub> emissions, with  
23 LDVs accounting for a substantial portion of these emissions. This paper aims to investigate  
24 the feasibility of zero-carbon fuels with focus on hydrogen and ammonia in spark ignition  
25 internal combustion engines for light-duty vehicles. With the increasing demand for  
26 sustainable and carbon-free mobility, alternative fuels such as hydrogen and ammonia are  
27 gaining attention as potential solutions. The properties and characteristics of these fuels and  
28 their potential for utilising them as a fuel in internal combustion engines are also reviewed.  
29 Current challenges and opportunities associated with the use of these fuels, including  
30 production, storage, and distribution, will be discussed. While there are still technical and  
31 infrastructural challenges that need to be addressed, hydrogen and ammonia have the  
32 potential to provide clean and efficient energy sources for light-duty vehicles. The  
33 development of these fuels, along with advancements in internal combustion engine  
34 technology, can help pave the way towards a carbon-free future for mobility.

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39 **Keywords**

40 Internal combustion engine, Zero carbon fuel, Spark ignition, Decarbonisation,  
41 Transportation.

## 42 **1. Introduction**

43 Global warming has become a serious environmental issue caused by the build-up of  
44 greenhouse gases in the atmosphere, mostly from the carbon dioxide emissions from the  
45 combustion products of fossil fuels. Among the major contributors, transportation is a  
46 significant contributor to this problem, responsible for 23% of global energy-related carbon  
47 dioxide emissions, according to the International Energy Agency<sup>1</sup>. Internal combustion  
48 engines (ICE) powered by fossil fuels, such as gasoline and diesel, are the primary source of  
49 carbon emissions in transportation. Road transportation alone accounts for 71.7% of carbon  
50 emissions from the transportation sector, as indicated by the European Environment Agency<sup>2</sup>,  
51 <sup>3</sup>. With the growth in the number of vehicles on roads worldwide, the level of carbon  
52 emissions is increasing, further compounding the challenges of climate change.

53 Battery electric vehicles (BEV) have emerged as a crucial technology to reduce emissions  
54 from road vehicles particularly in light-duty automotive applications, owing to their low  
55 refuelling and maintenance costs. However, some challenges of BEVs such as the high cost  
56 of the battery, long charging time and limited driving range present significant challenges to  
57 the widespread adoption of BEVs. Furthermore, it is essential to develop renewable energy  
58 sources and reduce coal and fossil power consumption for the future of BEVs, considering  
59 their life cycle<sup>4-7</sup>.

60 Charging infrastructure holds a crucial role in the electrification of transportation sector,  
61 given the costs of high-power charging infrastructure. There are two major types of charging  
62 system for BEVs, conductive and wireless charging. Currently, the majority of charging  
63 infrastructure is conductive charging, which requires a physical connection. Wireless  
64 charging offers a promising solution to enhance the efficiency and range of electric fleets.  
65 Catenary, traditionally linked with rail electrification, utilises overhead wires that supply

66 electric power to vehicles. By delivering continuous electric power directly from the  
67 infrastructure to the vehicle, catenary systems eliminate the need for large, heavy batteries,  
68 therefore reduce the overall weight of the vehicle and optimising energy consumption. This  
69 technology holds particular significance for urban settings, where frequent stops and starts  
70 can hinder the efficiency of traditional electric vehicles.

71 Currently, catenary charging infrastructure is especially relevant for road freight where load  
72 demand is higher<sup>8</sup>. Dynamic charging systems embedded in the road pavement or running  
73 along the side of the road, through overhead catenary power lines can also be used to directly  
74 power or charge BEVs<sup>9</sup>. However, the technology of dynamic charging is still in a  
75 developmental stage and requires considerable time before it can be implemented as a  
76 practical application.

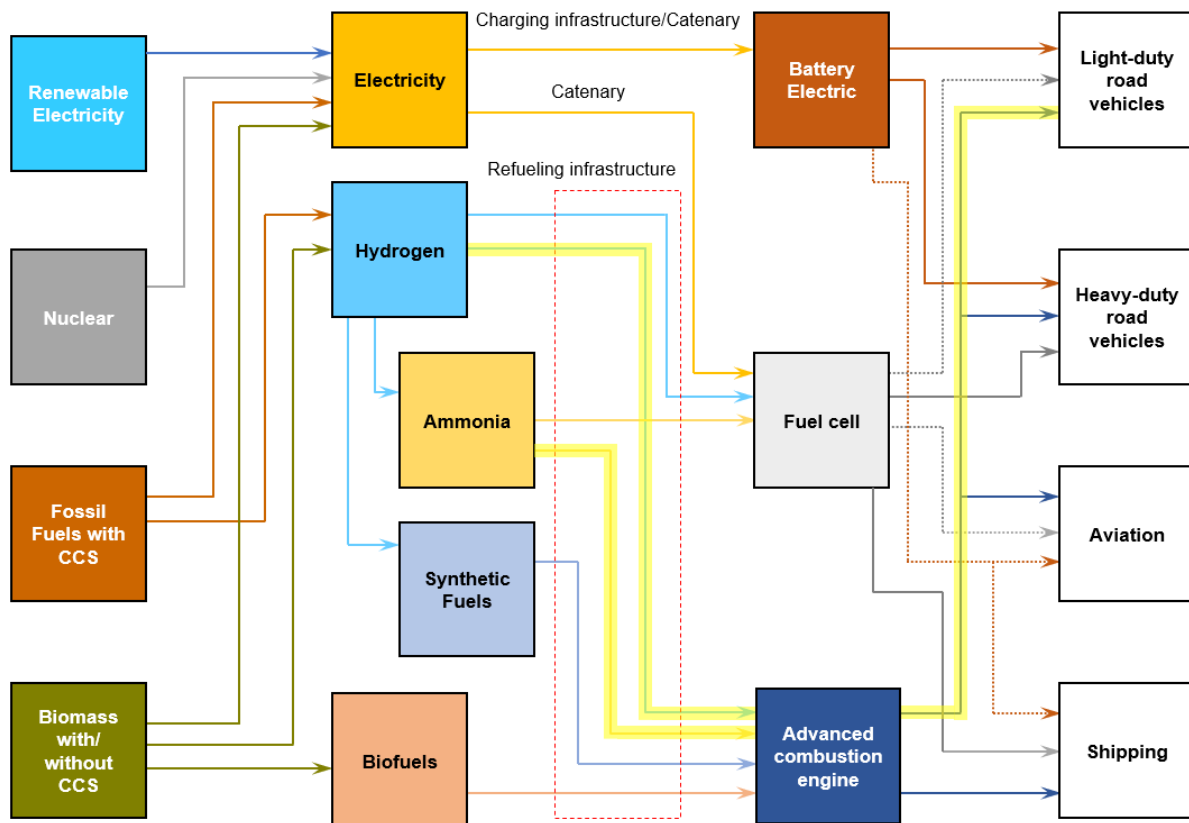
77 In addition, low-carbon electricity is vital for charging BEVs, as it leads to lower lifecycle  
78 greenhouse gas (GHG) emissions compared to vehicles powered by internal combustion  
79 engines<sup>10-12</sup>. These disadvantages of electric vehicles point out the continued dominance of  
80 ICE vehicles in the road transportation sector.

81 The vehicles used for transportation of passengers and goods can be separated into light-duty  
82 (LDV) and heavy-duty vehicles. LDVs are a significant contributor to the demand for fuel  
83 and therefore, GHG emissions. In the USA, LDVs are responsible for nearly half of the  
84 existing petroleum consumption and contributed approximately 1,000 million metric tonnes  
85 of CO<sub>2</sub>-equivalent GHG emissions in 2015, which accounted for approximately 16% of the  
86 country's overall GHG emissions<sup>13</sup>. Typically, most LDVs use gasoline fuel and spark  
87 ignition (SI) engines. With the global light-duty vehicle stock still increasing, alternative  
88 fuels became a key technology for a zero-carbon emission mobility future<sup>14</sup>.

89 To address the significant role of the transportation sector in carbon emissions, a transition  
90 towards cleaner and more sustainable forms of transportation is necessary. This includes the

91 utilisation of zero-carbon fuels in light-duty SI systems for automotive applications<sup>15</sup>. Zero-  
92 carbon fuels, which are generated from renewable sources, result in little to no net carbon  
93 emissions during their lifecycle, making them a cleaner alternative to fossil fuels<sup>16, 17</sup>. Zero-  
94 carbon fuels include biofuels, which are derived from biomass such as crops, waste materials,  
95 or algae, as well as hydrogen and ammonia that can be produced using renewable energy  
96 sources or from natural gas with carbon capture and storage technology<sup>18</sup>. These fuels hold  
97 the potential to substantially reduce carbon emissions in various industries, including  
98 transportation, where they can be used in ICEs, fuel cells, or other advanced propulsion  
99 systems. As a result, research and development efforts are focused on scaling up the  
100 production of zero-carbon fuels to meet the increasing demand for sustainable and low-  
101 carbon energy sources. Figure 1 provides a summary of the major pathways for low-carbon  
102 transport technology<sup>19</sup>.

103 Zero-carbon fuels have the potential to significantly reduce greenhouse gas emissions from  
104 LDVs, which are typically powered by ICEs fuelled by gasoline. In recent years, many  
105 advanced technologies have indicated the possibility of operating zero-carbon fuels in ICEs,  
106 make it feasible to use them in existing vehicles without requiring significant modifications.  
107 Nevertheless, challenges remain in terms of the cost and scalability of producing and  
108 distributing these fuels. Significant investments in infrastructure and technology development  
109 are required for producing zero-carbon fuels, as well as the availability of renewable energy  
110 sources at a large scale. Moreover, the limited availability of refuelling infrastructure for  
111 these fuels poses a barrier to their widespread adoption. Ultimately, the adoption of zero-  
112 carbon fuels in LDVs will depend on a range of factors, including technologies, policy  
113 support, and consumer acceptance. However, given the urgency of addressing climate  
114 change, the potential benefits of zero-carbon fuels make them a promising option for  
115 decarbonising the transportation sector and achieving a more sustainable future.



116

117 Figure 1. The energy pathway toward a net zero carbon mobility scenario, the highlighted lines  
 118 indicating the central aspects to be addressed in this study (Recreated from IPCC<sup>19</sup>)

119 This paper provides an assessment of the current state of zero-carbon fuels, specifically  
 120 hydrogen and ammonia, and their viability for use in light-duty spark-ignition vehicles. The  
 121 combustion properties and comparison of hydrogen and ammonia with common hydrocarbon  
 122 fuels for LDVs are summarised in Table 1. An overview of the various types of zero-carbon  
 123 fuels and their potential applications in the transportation industry is also provided. Some  
 124 challenges and opportunities linked to the production, distribution, and adoption of these  
 125 fuels are also discussed. Overall, the article aims to enhance our understanding of the  
 126 feasibility of zero-carbon fuels and emerging clean technologies for LDVs and emphasises  
 127 the need for further research and development in the field.

128

129 Table 1. Combustion properties of hydrogen and ammonia with other hydrocarbon fuels for LDVs<sup>20</sup>,  
 130 <sup>21</sup>.

Property	Ammonia	Hydrogen	Gasoline	Diesel
Chemical Formula	NH <sub>3</sub>	H <sub>2</sub>	C <sub>8</sub> H <sub>18</sub>	C <sub>12</sub> H <sub>23</sub>
Energy Density (MJ/kg)	18.6	120.1	44.4	42.8
Energy Density (MJ/L)	11.2 <sup>†</sup> 12.5 <sup>‡</sup>	0,010 – 0.011 <sup>†</sup> 8.49 <sup>§</sup>	32.8	35.8
Autoignition Temperature (°C)	651	572	246	210
Flame Speed (m/s)	0.32 - 0.40	1.5 - 2.1	0.3 - 0.5	0.25 - 0.3
Density (kg/m <sup>3</sup> )	0.771 <sup>†</sup> 600 <sup>‡</sup>	0.0899 <sup>†</sup> 70.8 <sup>§</sup>	750	835
Flammable Limit in Air (%)	15 – 28	4 - 75	1.4 - 7.6	0.6 - 5.5
Minimum Ignition Energy (mJ)	0.22 - 0.36	0.02 - 0.04	0.2 - 0.3	0.3 - 0.6

<sup>†</sup> Gaseous form under atmospheric pressure and 20°C

<sup>‡</sup> Liquified at 0.99 MPa temperature of 25°C

<sup>§</sup> Liquified at -252.9°C under atmospheric pressure

## 131 2. Hydrogen

132 Hydrogen is a clean energy source that holds great promise<sup>22</sup>. Theoretically, hydrogen fuel  
 133 generates no carbon emissions during combustion and can be produced from renewable  
 134 energy sources such as solar and wind power. Hydrogen can be used in various transportation  
 135 applications, including cars, buses, and trucks<sup>23</sup>. While some challenges remain, the use of  
 136 hydrogen fuel has the potential to promote sustainable and low-carbon transportation.

### 137 2.1. Hydrogen production

138 Hydrogen has been widely classified into different colour, depending on the production  
 139 method used and its environmental impact. To ensure scientific precision in this article these  
 140 main colours are supplemented with quantitative carbon intensity figures, as summarised in  
 141 Table 2. Currently the most common form of hydrogen is produced from fossil fuels such as

142 coal or natural gas without carbon capture technology, rendering it a non-zero-carbon fuel  
 143 with the highest carbon intensity of 11.57 kg CO<sub>2</sub>/kg H<sub>2</sub><sup>24, 25</sup>. Blue hydrogen also delivered  
 144 from fossil fuels also; however, it incorporates carbon capture technology, resulting in a  
 145 carbon footprint of 6.87 kg CO<sub>2</sub>/kg H<sub>2</sub>.

146 Table 2. Common hydrogen types, sources and the level of carbon emissions associated with the  
 147 production method.

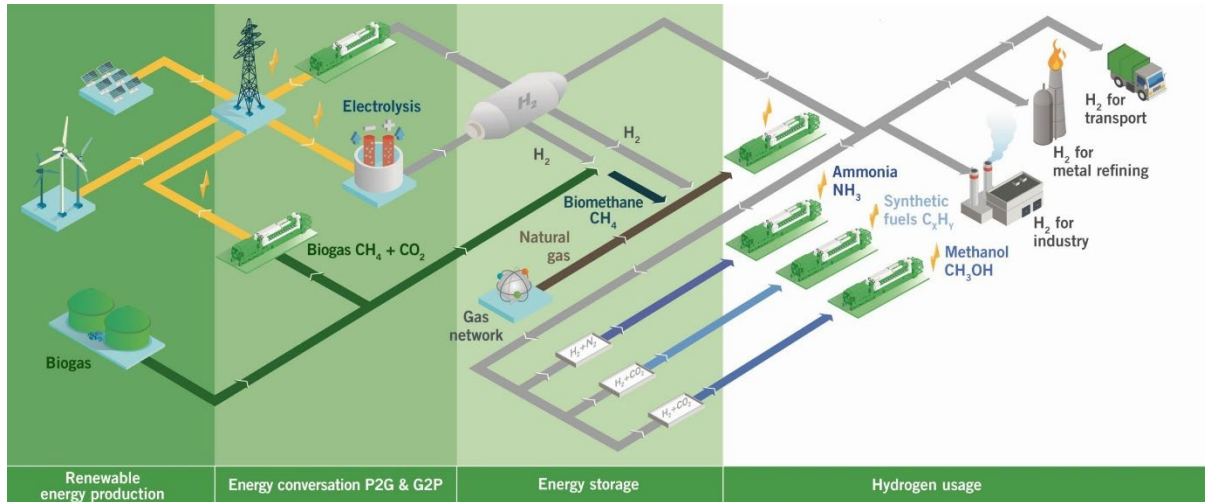
Hydrogen Type	Resource	Method	Technology	Carbon Emissions Level
Grey	Fossil fuels (natural gas, coal)	Steam methane reforming	No carbon capture technology	High
Blue	Fossil fuels (natural gas, coal)	Steam methane reforming	Carbon capture and storage	Moderate
Turquoise	Natural gas	Methane pyrolysis	Carbon capture and storage	Low
Green	Renewable energy (solar, wind)	Electrolysis	No carbon emissions	Zero

148 Turquoise hydrogen utilises methane pyrolysis, splitting methane into hydrogen and solid  
 149 carbon without releasing carbon dioxide. The carbon intensity of this type of hydrogen ranges  
 150 from 3.94 to 9.91 kg CO<sub>2</sub> /kg H<sub>2</sub> depending on the heat source for the process. Green  
 151 hydrogen, produced using renewable energy sources such as solar or wind power, is  
 152 considered the most environmentally friendly option<sup>26</sup>. However, green hydrogen production  
 153 is still in its early stages and is not yet widely available. Furthermore, it is noteworthy that if  
 154 the current grid electricity is used in electrolyser hydrogen production, it results in significant  
 155 carbon intensity of 34.85 kg CO<sub>2</sub>/kg H<sub>2</sub><sup>27</sup>.

156 Figure 2 illustrates the process of generating and storing hydrogen through blue and green  
 157 hydrogen pathways, which are both promising methods for producing zero-carbon hydrogen  
 158 fuel<sup>28</sup>. Blue hydrogen is produced from fossil fuels such as natural gas but utilises carbon  
 159 capture and storage technology to capture and store the carbon emissions. Green hydrogen,



160 on the other hand, is produced by electrolysing water into hydrogen and oxygen using  
 161 renewable energy sources such as wind or solar power. Both blue and green hydrogen have  
 162 potential to be used as a fuel for transportation, and there are ongoing projects aimed at  
 163 producing and storing these fuels for use in LDVs.



164

165 Figure 2. Hydrogen pathway toward sustainable energy production and utilisation (copyright Innio  
 166 Jenbacher, license no: 5619221468745, reproduced from ref.<sup>28</sup>)

167 The H2future project, supported by the European Union’s Horizon 2020 research  
 168 programme, is constructing the largest green hydrogen pilot facility in the world at the  
 169 Voestalpine site in Linz. The facility aims to produce CO<sub>2</sub>-free hydrogen for use in industry,  
 170 transportation, and energy. The system includes an electrolytic capacity of 6 MW, and the  
 171 ultimate goal is to produce hydrogen from electrolysed water with an efficiency of over  
 172 80%<sup>29</sup>. In the UK, investments in hydrogen technology are being made to reduce carbon  
 173 emissions in the transportation sector. Projects such as the hydrogen mini-grid system,  
 174 Gigastack, and Dolphyn demonstrate the entire industrial chain from hydrogen production to  
 175 energy utilisation, and the UK plans to produce green hydrogen through offshore wind farms.  
 176 The Gigastack project aims to deliver green hydrogen through a 5 MW electrolyser, and its  
 177 first phase has successfully developed the design and explored the industrial application of

178 the technology<sup>30</sup>. These projects demonstrate the potential of blue and green hydrogen as a  
179 viable zero-carbon fuel for the transportation sector.

## 180 **2.2. Hydrogen as a fuel in internal combustion engines**

181 Hydrogen has a long history of being used as a fuel in transportation. One of the earliest  
182 examples of a hydrogen powered ICE was De Rivaz's engine, invented by Francois Isaac de  
183 Rivaz in 1807. This engine utilised a mixture of hydrogen and oxygen, which ignited via an  
184 electric spark to produce power<sup>31</sup>. In 1820, Reverend W. Cecil introduced the Cecil gas  
185 engine, which used hydrogen and oxygen combustion to create a partial vacuum inside a  
186 cylinder. Although it was not very efficient and reliable, the Cecil engine demonstrated the  
187 potential of hydrogen as an alternative energy source<sup>32</sup>. Another notable example of a  
188 hydrogen vehicle was the Hippomobile, a three-wheel car powered by hydrogen gas invented  
189 by Etienne Lenoir in 1860<sup>33</sup>. Despite its potential, the development of hydrogen engines for  
190 transportation did not receive much attention until recently, due to the popularity of gasoline  
191 and diesel as fuels. The detail research of hydrogen as a fuel for ICE prior to 1990s was fully  
192 reviewed and reported in<sup>34,35</sup>.

193 In recent years, interest in hydrogen internal combustion engines (H2ICEs) has been renewed  
194 due to the need for cleaner transportation options. Hydrogen offers a promising substitute for  
195 traditional hydrocarbon fuel, given its ability to generate no greenhouse gas emissions,  
196 particularly when produced from renewable energy sources. One of the earliest examples was  
197 the Ford P2000, based on the Ford Focus model and using a modified internal combustion  
198 engine designed to run on hydrogen. The P2000 had a range of around 160 miles on a single  
199 tank of hydrogen and could reach a top speed of 85 miles per hour, with engine out NOx  
200 emissions ranging from 0.37 - 0.74 g/mile<sup>36</sup>. BMW produced the Hydrogen 7, a limited  
201 quantity car available for lease in select markets between 2006 and 2008<sup>37</sup>. Emission results

202 demonstrated that BMW Hydrogen 7 was probably the most environmentally friendly vehicle  
203 ever tested at the Argonne laboratory at that time<sup>38</sup>. Similarly, Mazda produced the RX-8  
204 Hydrogen RE in 2006, which also used a hydrogen-powered ICE<sup>39</sup>. However, both cars were  
205 expensive, had limited range, and required specialised refuelling infrastructure, limiting their  
206 practicality for most consumers.

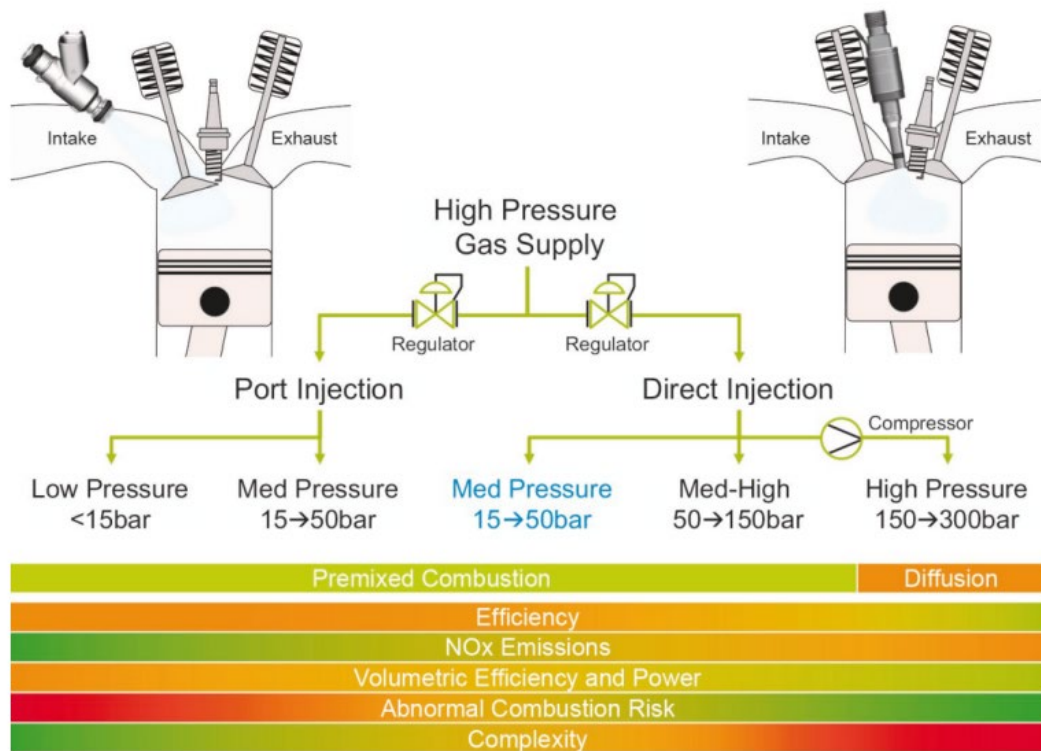
207 Toyota has recently announced plans to develop H2ICE versions of two popular models: the  
208 Corolla Sport and GR Yaris. The modified Corolla Sport was released in Japan in 2021<sup>40</sup>,  
209 while the modified GR Yaris followed in 2022<sup>41</sup>. Yamaha and Toyota are collaborating to  
210 develop a 5.0-liter V8 engine that runs on hydrogen fuel. This engine is based on the one  
211 used by the Lexus RC F coupe, but with modifications to its cylinder heads and fuel injectors,  
212 among other components. The engine is expected to deliver up to 450 hp of power at 6,800  
213 rpm and a torque of 540 Nm at 3,600 rpm<sup>42</sup>. This development highlights the potential for  
214 using hydrogen in high-performance vehicles that are also more environmentally friendly.

215 However, one of the major challenges in utilising H2ICEs in LDVs is the low density of  
216 hydrogen, which requires large storage tanks<sup>43</sup>. Nevertheless, there is still significant interest  
217 in hydrogen as a fuel for LDVs, as numerous ongoing research and development initiatives  
218 strive to improve the efficiency, cost-effectiveness, and sustainability of internal combustion  
219 engine vehicles<sup>44-51</sup>.

220 To fully capitalise on the potential of hydrogen as a fuel for LDVs, significant advances in  
221 fuel injection strategies must be made to optimise engine performance and reduce  
222 emissions<sup>52</sup>. This is because the unique properties of hydrogen, such as its high combustion  
223 speed and wide flammability range, require careful attention to the injection process to ensure  
224 efficient combustion and minimise emissions. Therefore, developing and implementing  
225 effective fuel injection strategies is essential for the successful integration of H2ICEs in  
226 LDVs.

### 227 **2.3. Injection strategy**

228 H<sub>2</sub>ICEs require different injection strategies due to hydrogen's high reactivity and different  
229 combustion characteristics compared to gasoline or diesel<sup>53</sup>. One commonly used strategy is  
230 port fuel injection (PFI), where fuel is injected into the intake port and mixed with the air  
231 before entering the combustion chamber. PFI systems are economical and straightforward to  
232 produce but have restricted control over the amount and timing of fuel injection. Another  
233 strategy is direct injection (DI), where fuel is directly introduced into the combustion  
234 chamber. DI systems allowing for more precise control over the fuel injection process  
235 resulting in higher fuel efficiency. However, DI systems are more complex and expensive to  
236 manufacture than PFI. Figure 3 illustrates a summary of hydrogen injection strategies ranged  
237 from low to high pressure as well as their advantages and disadvantages in ICEs<sup>54</sup>. With  
238 further research and development, hydrogen injection strategies can be optimised to improve  
239 engine performance, reduce emissions, and make hydrogen-fuelled LDVs more practical and  
240 cost-effective for consumers.



241

242 Figure 3. Hydrogen injection strategies (copyright Borg-Warner, license no: 5619230489053, adapted

243 from ref.<sup>54</sup>).

### 244 2.3.1. Port-fuel injection

245 Port fuel injection is the primary mixture injection strategy for H<sub>2</sub>ICE and is similar to a

246 traditional gasoline LDV engine. One advantage of hydrogen PFI is that it can utilise existing

247 engines, making the conversion to hydrogen combustion relatively easy<sup>55</sup>. Lee et al. used a

248 solenoid-driven gas valve to supply hydrogen to the PFI system, which can be easily adopted

249 in a conventional SI engine with simple modifications<sup>56</sup>.

250 To control the PFI of hydrogen in a H<sub>2</sub>ICE, Mathur and Das introduced timed manifold

251 injection. Their results indicated that a timed manifold injection system ensures the effective

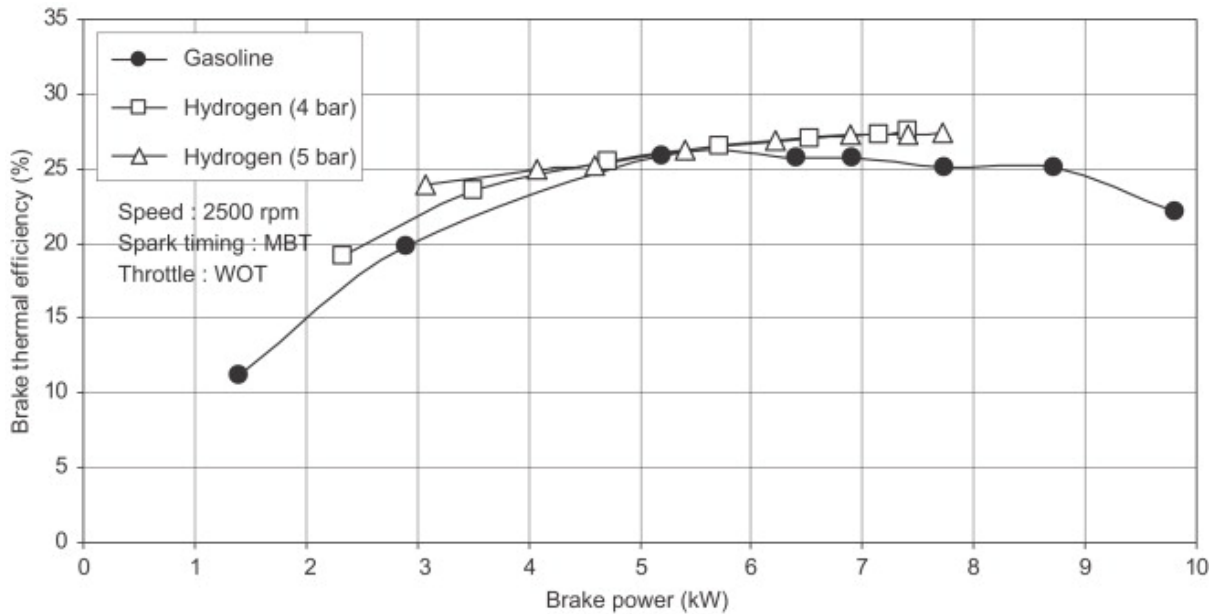
252 functioning of a hydrogen engine across the wide range of speeds and loads without any

253 abnormal combustion<sup>57</sup>. By implementing a suitable control system, the peak brake thermal

254 efficiency (BTE) of 27% (versus 25% for gasoline) under a wide range of operation can be

255 reached for hydrogen-fuelled engine (Figure 4)<sup>58</sup>. H<sub>2</sub>ICE with PFI can reach a peak indicated

256 efficiency of 45%, while the brake efficiency was 35%. Efficiency levels exceeding 30%  
 257 could be achieved over a wide range of operation conditions, presenting an improvement of  
 258 7-9% compared to gasoline within the same load range<sup>59</sup>. However, NOx emissions level is  
 259 significantly higher than that of gasoline operation.



260  
 261 Figure 4. Brake thermal efficiency of hydrogen combustion compared to base gasoline combustion  
 262 (License no: 5619230633788, reproduced from ref.<sup>58</sup>)

263 Pandey and Kumar conducted a study on the performance of PFI H2ICE with variable  
 264 compression ratio (VCR) technology. They found that under high compression ratio (CR) and  
 265 moderate equivalence ratio, brake power and BTE improved compared to gasoline. However,  
 266 as the lean limit decreased and CR increased, NOx emissions increased rapidly<sup>60</sup>. One way to  
 267 reduce NOx emissions from H2ICE is to control the throttle and excess air ratio. By applying  
 268 these measures, NOx emissions can be reduced to below 15 ppm in a naturally-aspirated  
 269 (NA) hydrogen engine, but this can limit torque and power due to backfire<sup>61</sup>. To achieve  
 270 backfire-free and low emissions without affecting engine performance, water injection, lean  
 271 burn technology and exhaust gas recirculation (EGR) can be utilised<sup>62, 63</sup>.

272 Combining PFI with water injection technology can result in a maximum power output of  
 273 78% compared with gasoline due to the reduction in of the amount of intake air displaced by  
 274 the hydrogen. Water injection also significantly reduces NOx levels without affecting BTE or  
 275 cyclic variation. However, it may cause adverse effects such as corrosion and lubricant  
 276 contamination<sup>64</sup>. Furthermore, lean burn and EGR strategies have been examined in the  
 277 cooperative fuel research (CFR) engine. The lean burn strategy was found to be more  
 278 effective in reducing NOx emissions under low load conditions, while both strategies were  
 279 equally effective for mid-load conditions<sup>65, 66</sup>.

280 Overall, a combination of PFI with water injection, lean burn and EGR strategies, can  
 281 effectively reduce NOx emissions while maintaining stable combustion in the H2ICE.  
 282 However, each strategy comes with its inherent advantages and disadvantages, and the  
 283 optimal combination may vary depending on the specific application and operating  
 284 conditions. Table 3 summarises the various strategies and their effectiveness in reducing NOx  
 285 emissions from the H2ICE.

286 Table 3. Summary of various operating strategies for hydrogen PFI engines<sup>65, 66</sup>.

Strategy	Advantages	Disadvantages
Water injection	<ul style="list-style-type: none"> <li>• Significantly reduces NOx emissions without affecting BTE and causes a small reduction in hydrocarbon (HC) emissions.</li> <li>• Effective in controlling knock.</li> <li>• Does not affect cyclic variation.</li> </ul>	<ul style="list-style-type: none"> <li>• May cause corrosion and lubricant contamination.</li> </ul>
Lean burn	<ul style="list-style-type: none"> <li>• Better efficiency than EGR strategy for low load conditions.</li> <li>• Very low NOx emissions; almost</li> </ul>	<ul style="list-style-type: none"> <li>• Poor efficiency of TWC under lean burn conditions.</li> </ul>

	<p>zero emissions when <math>\lambda \geq 3</math>.</p> <ul style="list-style-type: none"> <li>Nearly the same indicated power and indicated efficiency for mid-load conditions as stoichiometric with EGR.</li> </ul>	
EGR	<ul style="list-style-type: none"> <li>Highest indicated power output at mid and high load conditions.</li> <li>Lower NO<sub>x</sub> emissions than lean burn strategy for all load conditions.</li> <li>Possible to combine with supercharging for power increase.</li> <li>Can be varied to control NO<sub>x</sub> emissions.</li> </ul>	<ul style="list-style-type: none"> <li>Combustion instability at high EGR rates.</li> <li>Poor efficiency of TWC under EGR strategy with a stoichiometric mixture and variable EGR rates, due to lack of unburned hydrogen, which is used as a reductant.</li> <li>Only efficient under slightly rich conditions.</li> </ul>

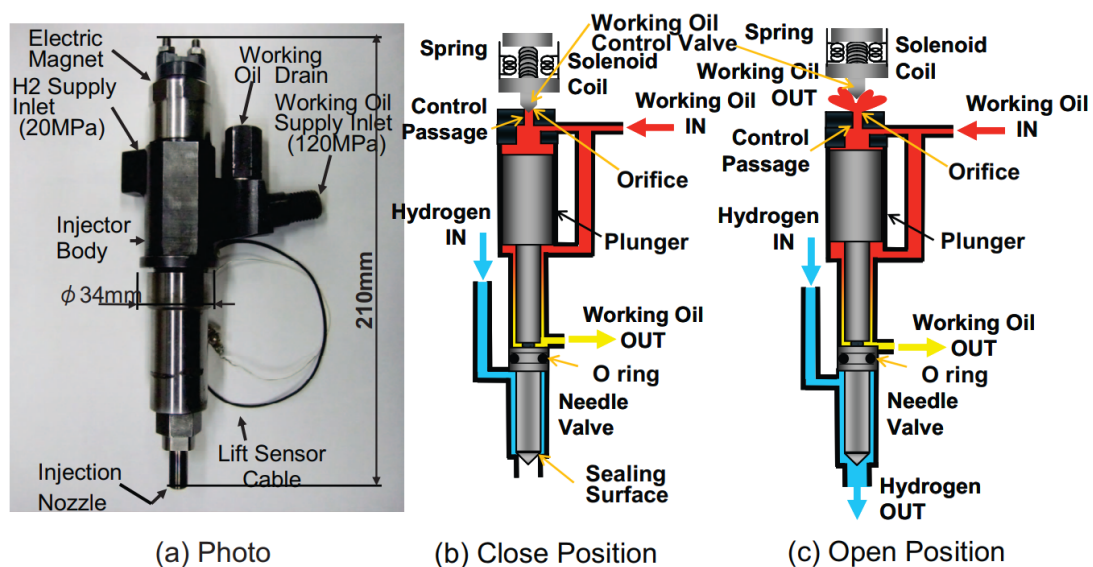
287 **2.3.2. Direct injection**

288 Direct injection of hydrogen in the ICEs is a promising technology for reducing greenhouse  
289 gas emissions and improving fuel efficiency. By directly injecting hydrogen into the  
290 combustion chamber, a more precise air-fuel mixture can be achieved, resulting in improved  
291 engine efficiency and lower emissions. The DI system also enables the use of higher CR,  
292 which can further improve engine efficiency<sup>67</sup>.

293 Gaseous hydrogen used in DI mode for LDV has shown great potential, particularly when  
294 high power density and instant power availability are required. Power output of hydrogen DI  
295 operation can potentially improve by approximately 17% higher than the PFI of gasoline<sup>68</sup>.  
296 Under part load operation with lean mixture, it was observed that 40% indicated thermal  
297 efficiency (ITE) with zero engine out emissions can be achieved, while a stoichiometric

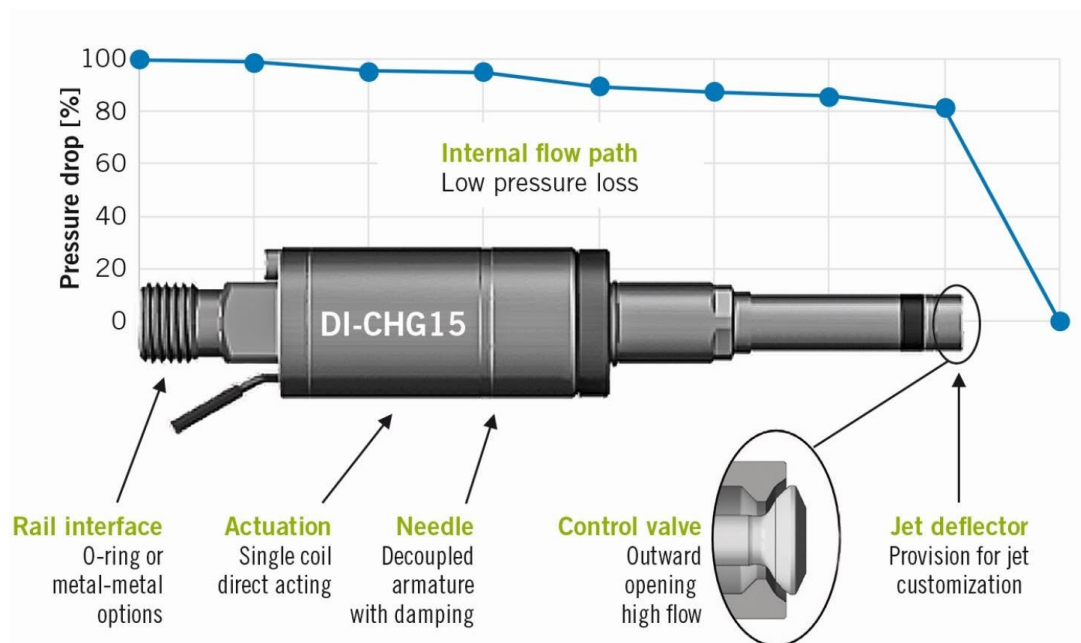


298 mixture allows for high power density, but a catalyst is required to avoid NOx emissions.  
 299 Compared to PFI, hydrogen DI results in a higher energy contained of the mixture in the  
 300 cylinder, which can be used to produce higher power output<sup>69</sup>.  
 301 Despite its potential for improving fuel efficiency, the adoption of hydrogen DI technology in  
 302 LDV is limited by the lack of widely available direct injectors for hydrogen. This is due to  
 303 the unique properties of hydrogen that require different injector designs than those used for  
 304 conventional gasoline or diesel fuel injection<sup>70</sup>. Furuhashi and Kobayashi<sup>71</sup> demonstrated the  
 305 potential of DI by showing that injecting low temperature liquid hydrogen into an engine can  
 306 increase its maximum output by 20-25% compared to gasoline engines and backfire can be  
 307 completely prevented.  
 308 Yamane et al.<sup>72</sup> have successfully developed compact hydrogen gas injectors with high-  
 309 pressure, highly responsive, and capable of injecting at high rates. Figure 5 illustrates the  
 310 structure and working mechanism of the developed gaseous hydrogen direct injector.  
 311 However, further research is required to evaluate the reliability and durability of these  
 312 injectors for practical vehicle application<sup>73</sup>.

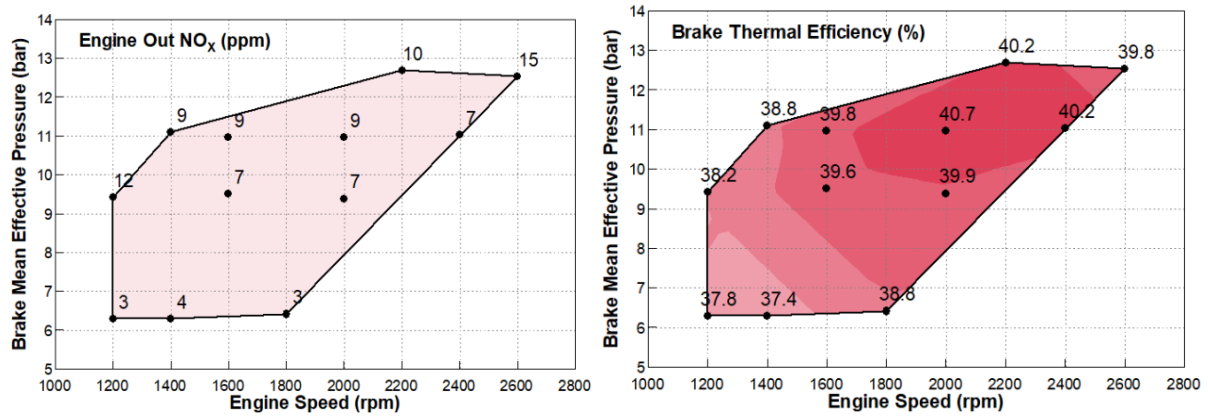


313 (a) Photo (b) Close Position (c) Open Position  
 314 Figure 5. Gaseous hydrogen direct injector design and working mechanism (License ID: 1392081-1,  
 315 adapted from ref.<sup>72</sup>).

316 BorgWarner has designed a direct injector specifically for hydrogen, which is able to operate  
 317 at high pressures and handle the unique characteristics of hydrogen fuel, such as its low  
 318 density and high flammability (Figure 6). The hydrogen direct injector has been successfully  
 319 used in a 1.6 L Hyundai SI engine made for a commercial vehicle, achieving a maximum  
 320 BTE of 40.7% at 2000 rpm and 140 Nm. Furthermore, NO<sub>x</sub> emissions were found to be  
 321 lower than 15 ppm and 0.2 g/kWh throughout the entire range of operation (Figure 7)<sup>74, 75</sup>.  
 322 The hydrogen direct injector has also evaluated by Atkins et al. in a modified Ricardo Proteus  
 323 single cylinder research engine. The results demonstrated that with lean combustion and  
 324 cooled EGR, engine out NO<sub>x</sub> emissions could be kept very low, with levels below 10 ppm<sup>76</sup>.  
 325 Moreover, Liebherr has introduced new injection concepts specifically designed for hydrogen  
 326 engines, which can be utilised in both on and off-road applications<sup>77-79</sup>.



327  
 328 Figure 6. High pressure direct injector and its structure for hydrogen application (copyright Borg-  
 329 Warner, license no: 5619231423986, adapted from ref.<sup>54</sup>).

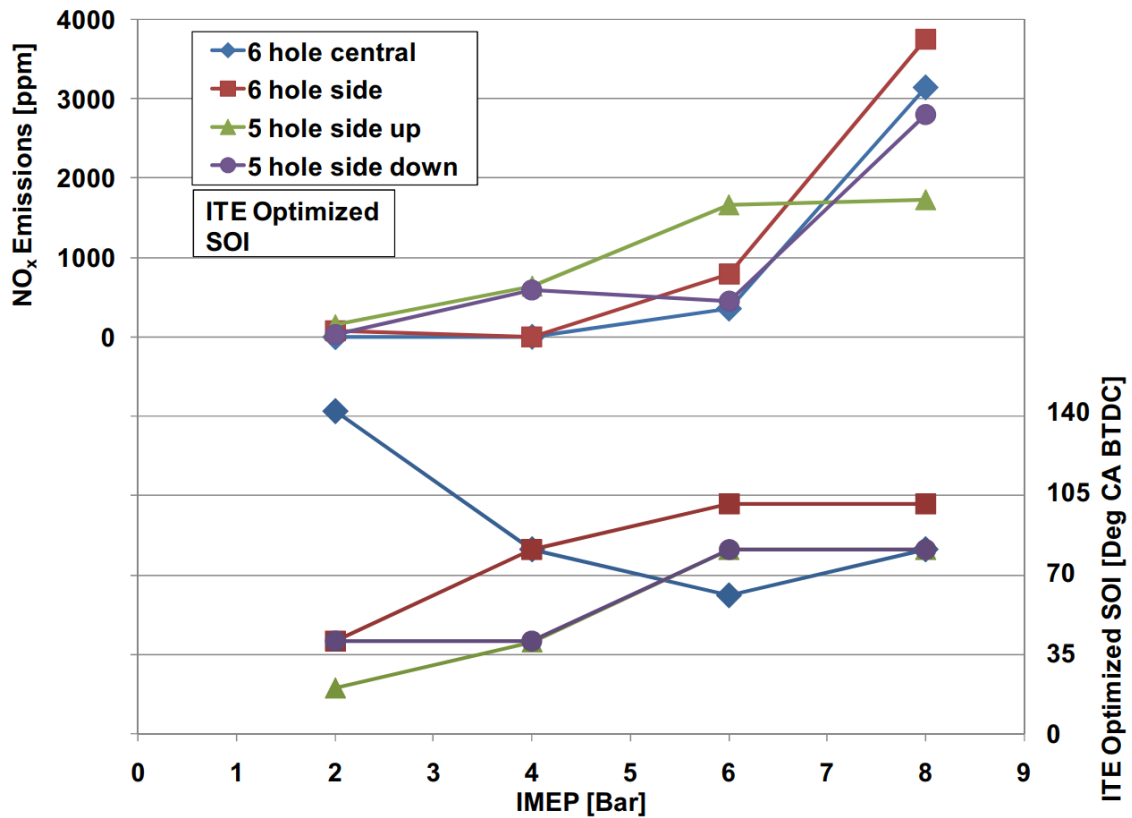


330

331 Figure 7. The engine out emissions and brake thermal efficiency of 1.6 L Hyundai hydrogen SI engine  
 332 (Reproduced from ref.<sup>75</sup>, CC-BY)

333 The mixture formation is a critical factor in DI systems, as it directly impacts engine  
 334 performance and emissions. However, due to the high reactivity of hydrogen, it is susceptible  
 335 to pre-ignition and backfire, which can be managed through injection control. Injection of  
 336 hydrogen during the intake stroke prevents backfire but reduces power out and thermal  
 337 efficiency due to engine knock. Injection during the compression stroke prevents knock and  
 338 increases thermal efficiency and maximum output power. Late injection during the  
 339 compression stroke results in noteworthy emissions reduction, primarily attributed to lean  
 340 operation during instances of high load conditions<sup>80</sup>.

341 Moreover, the nozzle design and the injector location for DI have a significant impact on ITE  
 342 at low load conditions. Injectors located on the side show higher efficiency compared to  
 343 central locations. However, at high loads, the impact of injector location and nozzle design is  
 344 much smaller. The NO<sub>x</sub> emissions exhibit contrasting patterns when comparing low loads to  
 345 high loads, but the general trends relative to the start of injection timing remain consistent  
 346 across a range of load points, regardless of injector nozzle design, as indicated in Figure 8<sup>81</sup>.



347

348 Figure 8. NOx emissions and the optimised start of injection timing as a function of engine load for  
 349 various injector nozzle design in a hydrogen DI engine (License ID: 1392085-1, reproduced from  
 350 ref.<sup>81</sup>).

351 Various injection strategies have been investigated to further improve the potential of  
 352 hydrogen DI. It is possible to maintain engine efficiency while reducing NOx emissions by  
 353 using multiple injection strategies in a single-cylinder hydrogen engine with high-pressure  
 354 direct injection<sup>82, 83</sup>. Injection timing also plays a significant role in combustion and  
 355 emissions of H2ICE. Retarding the fuel injection timing can increase the intake air flow rate,  
 356 decrease NOx emissions, and potentially improve efficiency. Increasing the fuel injection  
 357 pressure may allow for further retardation, but it may also increase combustion speed and  
 358 temperature, decreasing efficiency. The optimal injection timing may also depend on the air-  
 359 to-fuel ratio and combustion conditions, with a mixture near the stoichiometric ratio  
 360 potentially providing the highest torque<sup>84</sup>.

## 361 **2.4. Challenges with hydrogen fuel**

362 As mentioned above, while hydrogen fuel offers many potential benefits but there are also  
363 several challenges that need to be addressed for widespread adoption.

364 First of all, the producing cost of green hydrogen fuel is higher than conventional  
365 hydrocarbon fuels such as gasoline and diesel, primarily due to the high cost of electricity  
366 required for the electrolysis process. Additionally, the infrastructure required for producing,  
367 transporting, and storing hydrogen is not yet widely available.

368 Secondly, the density of hydrogen gas is only  $0.090 \text{ kg/m}^3$  at standard temperature and  
369 pressure, which is much lower than traditional fuels. This results in hydrogen taking up more  
370 space and requiring high pressure storage or extremely low temperatures for efficient storage.  
371 This makes it difficult to store and transport large quantities. Several solutions are being  
372 explored to address the problem of hydrogen storage such as compressed gas storage which is  
373 the most common method of storing hydrogen<sup>85</sup> and liquid storage, which can store hydrogen  
374 as a cryogenic liquid at extremely low temperatures ( $-253^\circ\text{C}$ ). However, the cost of  
375 liquefying hydrogen and the need for cryogenic storage equipment make this option less  
376 practical<sup>86</sup>. Solid-state hydrogen storage using materials such as metal hydrides is also being  
377 investigated<sup>87</sup>. One promising method is using ammonia or methanol as a hydrogen carrier,  
378 which can be easier to handle and transport, but requires additional processing to release the  
379 hydrogen.

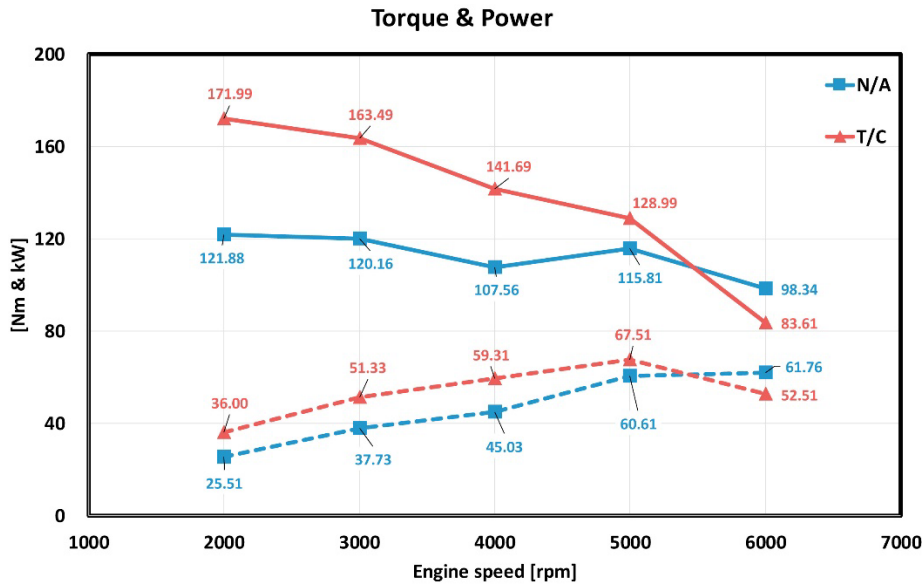
380 While hydrogen fuel itself produces no carbon emissions, the current production process of  
381 hydrogen heavily relies on fossil fuels (i.e., grey hydrogen). Until renewable energy sources  
382 can be used to produce green hydrogen more efficiently, the overall carbon emissions  
383 associated with hydrogen fuel may not be significantly lower than traditional fuels. In  
384 addition, due to the high combustion temperature, H<sub>2</sub>ICE produce NO<sub>x</sub> emissions, which

385 leads to the formation of thermal NO<sub>x</sub>. To reduce NO<sub>x</sub> emissions, various methods such as  
386 EGR, lean-burn combustion, and catalytic converters can be applied.

387 Moreover, hydrogen has a low density and a high diffusivity, which means it tends to mix  
388 with air quickly but can also easily separate from the air, resulting in a non-uniform mixture.  
389 This can lead to combustion instability, which can cause engine knock, misfire, and reduced  
390 power output. To enhance the power output of H<sub>2</sub>ICE, one approach is to increase the CR of  
391 the engine. The low energy density and higher octane rating under lean combustion compared  
392 to gasoline allows a high CR in the engine to be used<sup>88</sup>.

393 Another approach to increase H<sub>2</sub>ICE power output is to use boosting devices to increase the  
394 air mass flow rate entering the engine, allowing for a larger amount of hydrogen to be burned.  
395 The Ultra Boost for Economy project demonstrated that the fuel consumption of the boosted  
396 engine can be reduced by 23% with the same power output as baseline engine<sup>89</sup>. Boosting a  
397 hydrogen engine with a turbocharger can increase torque and power by 41% compared to a  
398 NA engine (Figure 9)<sup>90</sup>. Further improvements could be achieved by boosting the engine with  
399 supercharger, which can result in a 30% of BTE and 50% of ITE<sup>63, 91-93</sup>.

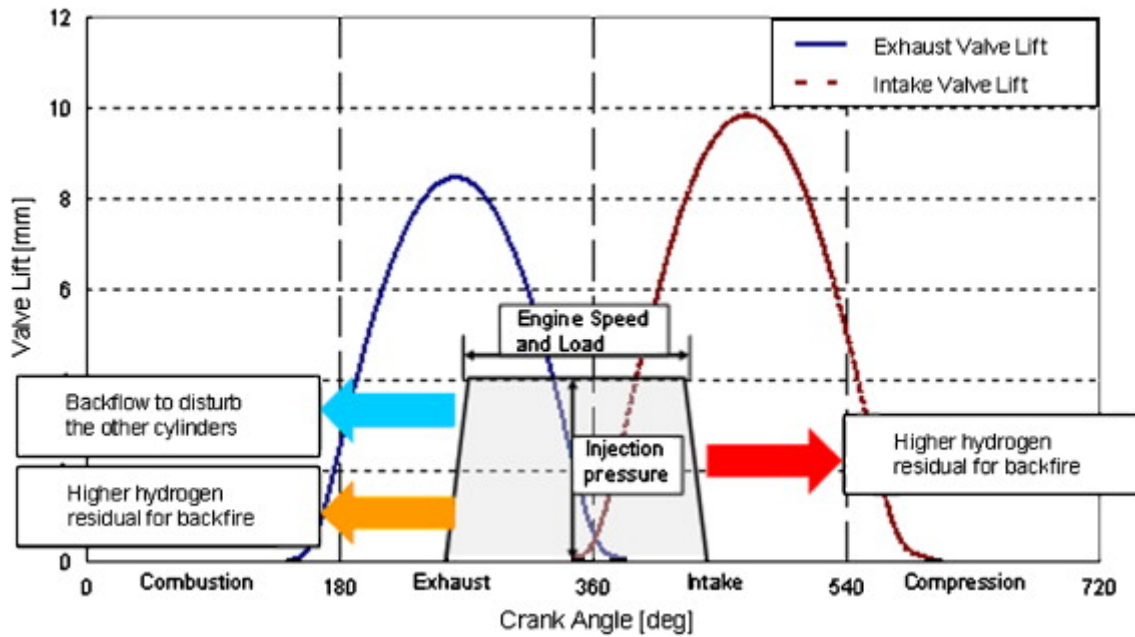
400 The pre-chamber is a promising method for enhancing power output, as demonstrated in  
401 conventional engines<sup>94-97</sup>. Simulation results show that a SI engine with a pre-chamber  
402 installed operating under lean conditions provides higher ITE compared to the normal SI  
403 mode<sup>98</sup>. Adding hydrogen to a single cylinder engine with a pre-chamber increased the  
404 efficiency, gross work, and indicated mean effective pressure (IMEP), while also improving  
405 combustion quality and reducing CO and UHC emissions by 20% and 15%. However, NO<sub>x</sub>  
406 emissions increased by approximately 14%<sup>99</sup>. While the pre-chamber has shown promising  
407 results, it is a relatively new concept for H<sub>2</sub>ICE that requires further investigation to fully  
408 understand its potential benefits and limitations.



409

410 Figure 9. Effect of turbocharger on hydrogen engine torque and power output (License no:  
411 5619240462019, reproduced from ref.<sup>90</sup>).

412 Another challenge associated with H2ICE is the risk of backfire or flashback. Hydrogen has a  
413 wide flammability range and a low ignition energy making it easy to ignite in the intake  
414 manifold or the injector, leading to a flame that propagates back into the injector. This can  
415 cause damage to the injector, resulting in engine damage or failure. Figure 10 shows a  
416 correlation between the injection configuration and potential occurrence of backfire<sup>100</sup>. One  
417 method to prevent backfire in a hydrogen engine is to adjust the air-fuel ratio to a lean  
418 mixture, reducing the risk of unburned hydrogen igniting in the intake manifold or exhaust  
419 system<sup>101</sup>. Another method to prevent backfire is to use a cold-rated spark-plug with proper  
420 ignition timing and ensuring proper fuel injection<sup>102-104</sup>. Optimising spark timing in  
421 combination with water injection can also reduce the chances of backfire and improve the  
422 power output of H2ICE<sup>62, 105, 106</sup>.



423

424 Figure 10. The correlation between the hydrogen injection configuration and the potential occurrence  
 425 of backfire (License no: 5619240658087, adapted from ref.<sup>100</sup>)

426 Finally, the injection of hydrogen requires a highly pressurised fuel system to deliver the fuel  
 427 to the injectors, which can be complex and costly to design and maintain. The high pressure  
 428 also increases the risk of leaks and can lead to safety concerns.

### 429 3. Ammonia

430 Ammonia is an alternative fuel that has gained interest due to its zero-carbon emissions and  
 431 potential for production from renewable sources such as wind and solar power. It is a  
 432 colourless gas with a pungent odour and can be conveniently stored and transported in liquid  
 433 form under moderate pressure. Owing to its significant hydrogen content, ammonia holds  
 434 promises as a fuel for internal combustion engines. Nevertheless, utilising ammonia as fuel  
 435 comes with challenges including its toxicity, corrosiveness, and the requirements for  
 436 specialised handling and storage infrastructure<sup>107</sup>.



### 437 3.1. Ammonia production

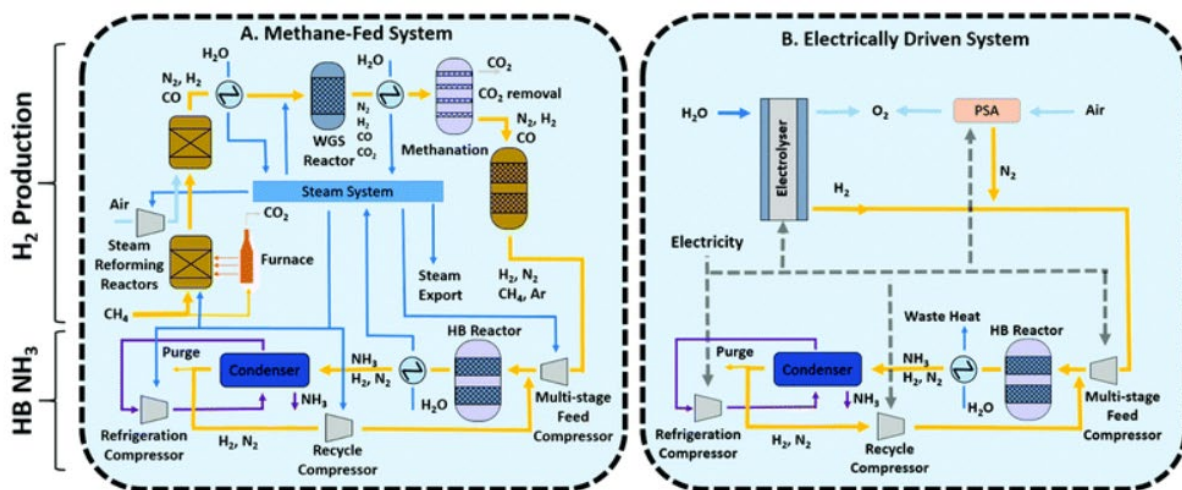
438 At present, ammonia is primarily produced through the Haber-Bosch process. This technique  
439 includes the combining of nitrogen and hydrogen reaction with an iron-based catalyst under  
440 high pressure (typically around 200 atm) and temperature (around 450°C)<sup>108</sup>. The nitrogen is  
441 typically obtained from the atmosphere by means of air separation, while hydrogen can be  
442 produced from a variety of sources including natural gas, coal, or electrolysis of water.  
443 However, the Haber-Bosch process is energy-intensive, requiring a significant amount of  
444 fossil fuel input and contributing to around 2% of global GHG emissions<sup>109-111</sup>.  
445 Therefore, there is a need for greener methods of ammonia production that are more energy-  
446 efficient and environmentally friendly. Some alternative production methods include  
447 electrochemical synthesis, which uses renewable electricity to convert nitrogen and water into  
448 ammonia<sup>112</sup>, and biological processes that utilise microorganisms to produce ammonia<sup>113</sup>.  
449 Another method of ammonia production is the hydrogenation of atmospheric nitrogen which  
450 uses renewable energy sources to produce hydrogen and then combines it with nitrogen in the  
451 presence of a catalyst to produce ammonia<sup>114</sup>. This process holds the potential to diminish  
452 GHG emissions associated with ammonia production, as it relies solely on renewable energy  
453 sources and thus avoids the need for fossil fuel inputs. Plasma-assisted synthesis involves the  
454 use of an electrical discharge to break apart nitrogen and hydrogen molecules, which then  
455 recombine to form ammonia<sup>115</sup>. Table 4 provides a concise overview and comparison of  
456 different methods for NH<sub>3</sub> production.

457 Table 4. Comparison of various ammonia production methods

Production Method	Advantages	Disadvantages
Haber-Bosch process	Mature technology, large-scale production capability.	Energy-intensive, and thus conventionally requires fossil fuel

		input, contributes to greenhouse gas emissions.
Hydrogenation of N <sub>2</sub>	Uses renewable electricity as a power source, low carbon footprint.	Technology still in development, low production capacity, high capital and operational costs.
Plasma-assisted synthesis	Can use renewable electricity, high production rate.	High energy consumption, requires additional equipment, expensive catalysts.
Electrochemical synthesis	Low energy consumption, can use renewable electricity.	Technology still in development, low production capacity, expensive catalysts.
Biomass gasification	Uses renewable feedstock, potential for carbon neutral production.	Requires significant amounts of biomass, low production rate, impurities in feedstock can affect catalysts.

458 Alternative methods of ammonia production offer several advantages over the traditional  
459 Haber-Bosch process in terms of production rate without relying on fossil fuel. Nevertheless,  
460 they encounter significant challenges, including the high expenses associated with selective  
461 and efficient catalysts. Therefore, the production of ammonia still heavily depends on the  
462 traditional process but with a transition towards more advance, sustainable and  
463 environmentally-friendly approaches, such as switching from methane-based hydrogen  
464 source to renewable ones<sup>116</sup>. The “green Haber-Bosch” approach, which utilises electrolysis  
465 to produce hydrogen from water using renewable electricity sources<sup>117</sup>. Figure 11 provides a  
466 simplified schematic of traditional and converted ammonia production process<sup>111</sup>.



467

468 Figure 11. Schematic diagram of the traditional Haber Bosch process (A) utilising methane and (B)  
 469 an electric-powered alternative (Reproduced from ref.<sup>111</sup> with permission from the Royal Society of  
 470 Chemistry).

### 471 3.2. Ammonia as a fuel for internal combustion engines

472 Ammonia for some time has been considered as a promising alternative fuel for ICEs due to  
 473 its high hydrogen content, and high octane rating. One of the advantages of ammonia as a  
 474 fuel is that it can be easily stored and transported, making it a more practical from  
 475 hydrogen<sup>118</sup>. In fact, ammonia powered buses were introduced and used in Belgium in 1943  
 476 due to the shortage of hydrocarbon-based fuel during World War II<sup>119</sup>. A military application  
 477 of an ammonia vehicle was introduced in the US in 1965<sup>120</sup>.

478 In the mid-1960s, research focused on modifying existing engines to operate on ammonia  
 479 fuel and developing new engines specifically for ammonia. Garabedian and Johnson  
 480 discussed the challenges of converting engines to operate solely on ammonia, as well as the  
 481 potential benefits of savings in weight, volume, cost, and complexity<sup>121</sup>. Although the results  
 482 of these experiments were generally positive, ammonia faced significant challenges to  
 483 widespread adoption as a fuel. One major challenge was the need for costly and impractical  
 484 modifications to existing engines. Another challenge was the increased fuel requirements for

485 ammonia, which would have required larger and heavier fuel tanks, compromising vehicle  
486 performance<sup>122-126</sup>. Additionally, the availability of cheap gasoline and the lack of  
487 infrastructure for producing and distributing ammonia led to the decline of ammonia-powered  
488 vehicles.

489 Utilising ammonia as a fuel in spark ignition engines for LDV has some challenges due to its  
490 low energy density and high autoignition temperature. Achieving stable combustion is one of  
491 the main challenges of ammonia SI engines due to its low flame speed and narrow  
492 flammability range<sup>127</sup>. To overcome these challenges, several modifications are necessary to  
493 the fuel, ignition, and exhaust system. Ammonia must be stored in a high-pressure tank, and  
494 the fuel system must be adapted to accommodate the different fuel properties of ammonia  
495 compared to conventional fuel. The ignition system must be modified to provide a high-  
496 energy spark to initiate the combustion process, and the exhaust system must be modified to  
497 handle the different exhaust gases produced by ammonia combustion<sup>128</sup>.

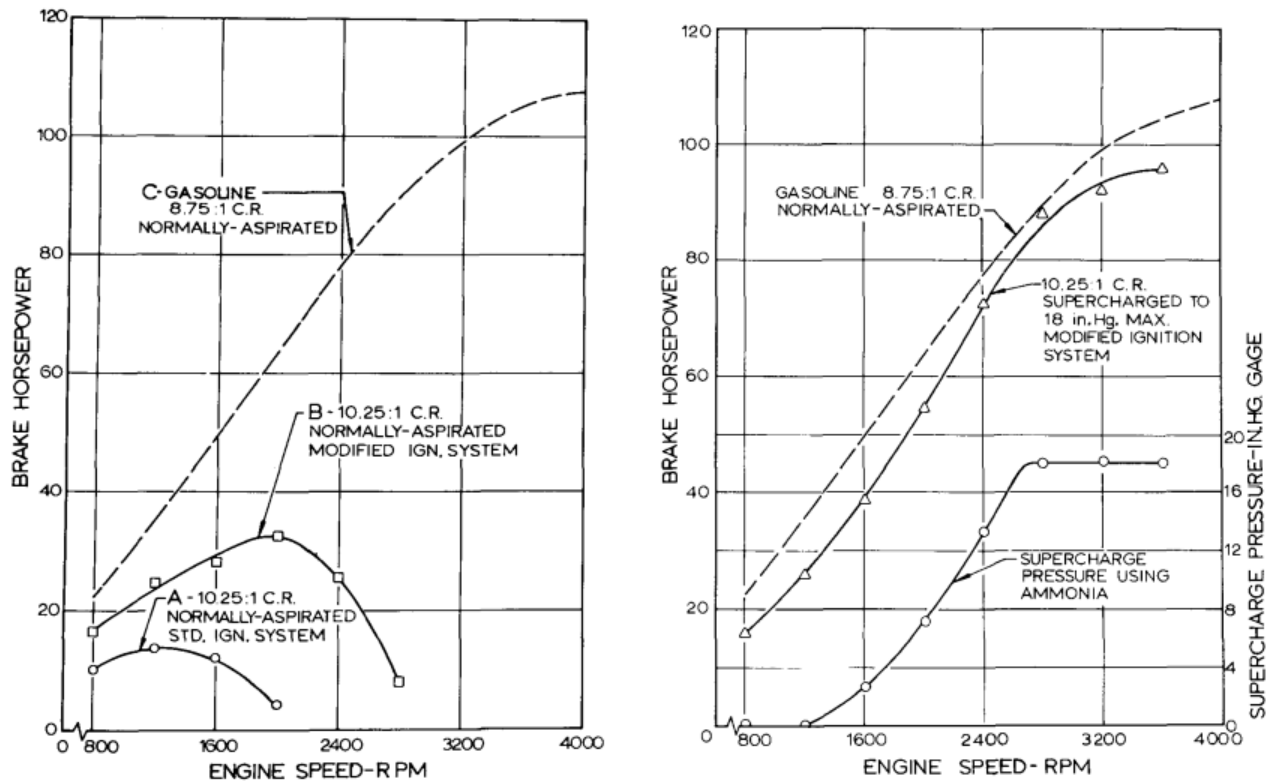
498 One approach to using ammonia in SI engines involves using it as a partial replacement for  
499 conventional fuel, by mixing with gasoline or natural gas in varying ratios and tuning the  
500 engine to operate on this fuel mixture. Although this approach can reduce emissions and  
501 improve fuel efficiency, it requires modifications to the fuel and ignition system. Another  
502 approach is to use hydrogen as a combustion promoter in dedicated SI engines that are  
503 designed specifically to operate on ammonia. These operation modes allow higher CR,  
504 advanced ignition timing, and other parameters to be optimised to improve the engine  
505 combustion process and overall performance<sup>129</sup>.

506 Ongoing research on ammonia as a fuel in SI engines is making it more feasible with  
507 advances in technology and engine design<sup>130</sup>. The following section will discuss the  
508 feasibility of ammonia fuel in different operation modes including ammonia-only and dual-  
509 fuel with focuses on ammonia and hydrogen blends.

### 510 **3.2.1. Ammonia-only engines**

511 There have been only a few studies conducted on spark ignition engines operating solely on  
512 ammonia. Starkman et al.<sup>126</sup> found that little modification is needed to use ammonia in SI  
513 combustion if it is introduced in vapour form and undergoes partial decomposition into  
514 hydrogen and nitrogen. The engine maximum output reached 70% of gasoline-fueled engines  
515 and could exceed that if the ammonia were introduced as a liquid. However, Cornelius et al.  
516 reported that the use of ammonia only as a fuel resulted in unstable and poor performance.  
517 Nevertheless, increasing the spark energy, compression ratio, and applying a supercharger  
518 can significantly improve engine combustion and power output, as indicated in Figure 12.  
519 The peak brake power achieved with an ammonia engine was approximately 10% lower than  
520 the maximum engine power attained with gasoline<sup>122</sup>. Additionally, Pearsall successfully  
521 developed an ammonia burning engine with a 10.26:1 CR by modifying the ignition coil,  
522 spark plug, fuel delivery system and cylinder head. When operated at 4000 rpm the engine  
523 provided 53 hp while it generated 68 hp on gasoline. However, it was not possible to use a  
524 higher compression ratio because peak cylinder pressures were too high, resulting in  
525 crankshaft failure<sup>131</sup>.

526 The limited research in this area is partly due to the lower energy density of ammonia  
527 compared to conventional fuels. Additionally, the combustion of ammonia in a spark-ignition  
528 engine presents challenges related to ignition timing and combustion stability. However, with  
529 the growing focus on zero-carbon transportation, there has been a revived interest in  
530 exploring the potential of ammonia as a viable alternative fuel for SI engines.

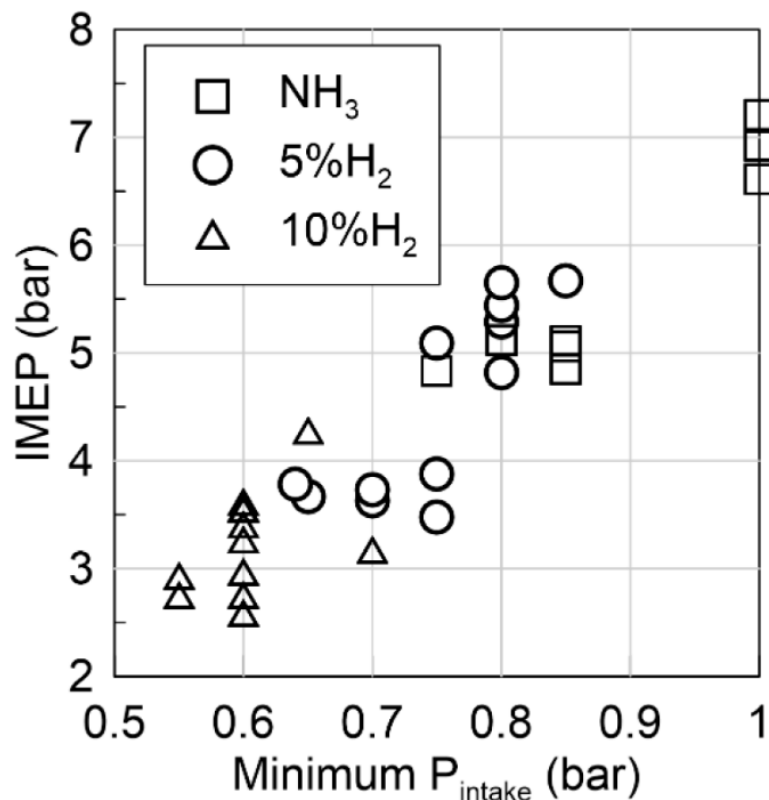


531

532 Figure 12. Performance of a multi-cylinder engine operating on ammonia and gasoline, under full-  
 533 throttle with normally aspirated conditions and modified ignition systems (left); the same engine with  
 534 supercharging and a modified ignition system (right) (License ID: 1392090-1, reproduced from  
 535 ref.<sup>122</sup>)

536 In order to utilise the direct injection in ammonia applications and achieve similar spray  
 537 characteristics to gasoline, certain conditions must be met, including an atmospheric  
 538 temperature and pressure at 20°C and 7 bar, as well as the injection duration is well below 1.2  
 539 ms, due to the ammonia reaches the wall after this certain duration<sup>132</sup>. To achieve ammonia  
 540 combustion without engine modifications and preheating the air, the engine must be warmed  
 541 up before gradually introducing ammonia. This has been achieved by using methanol as a  
 542 fuel first<sup>133</sup>. Eventually, a full shift transition from methanol to ammonia could be achieved  
 543 and the highest power output of engine with a CR of 15:1 using liquid ammonia was  
 544 approximately 60% compared to that achieved with gasoline at 9:1 CR<sup>133</sup>. However, Mørch  
 545 et al.<sup>134</sup> found that it was possible to operate the engine with CR varied from 6.23 to 13.58

546 using pure ammonia fuel but this resulted in unstable combustion and a tendency to cut out.  
 547 Lhuillier et al.<sup>135</sup> conducted a study on the performance of ammonia in a GDI engine, and  
 548 their results suggested that near-stoichiometric lean operation is recommended to mitigate  
 549 NOx and NH<sub>3</sub> emissions while maintaining satisfactory power output and efficiency. The  
 550 operating limit of ammonia in SI engines was also investigated and results indicate that a  
 551 minimum intake pressure of 0.75 bar (equivalent to 4.8 bar of IMEP) is sufficient for  
 552 ammonia combustion under conditions of low engine speeds and loads (as shown in Figure  
 553 13)<sup>136</sup>.



554  
 555 Figure 13. Operating limit and IMEP of an ammonia engine with various amounts of hydrogen  
 556 addition (Adapted from ref.<sup>136</sup>, CC-BY)

557 Due to the slow laminar burning rate of ammonia, operating an engine at higher speed (above  
 558 2000 rpm) without boosting or modifying is not possible<sup>136</sup>. Laminar burning velocity and  
 559 turbulent expanding flame measurements were conducted and presented in the study by

560 Lhuillier et al. study, but this was insufficient to explain the engine combustion behaviour.  
561 Therefore, further investigations, including experimental and simulation works, are needed to  
562 gain a deeper understanding of pure ammonia combustion and to optimise practical  
563 combustion systems<sup>137</sup>.

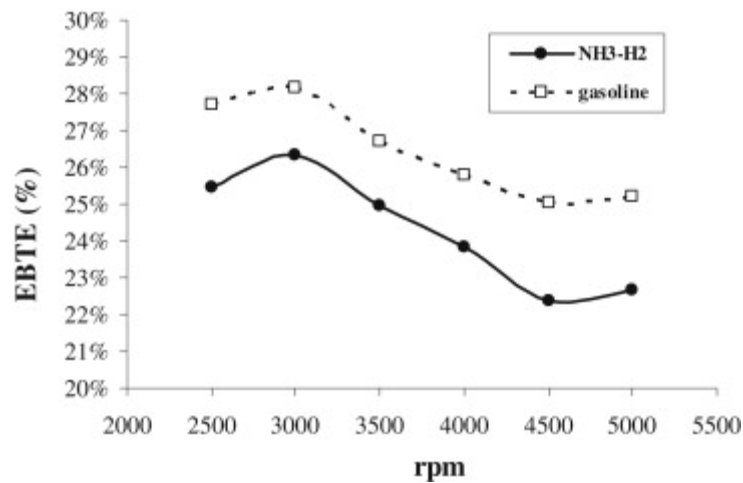
### 564 **3.2.2. Ammonia dual fuel engines**

565 There is a widespread belief that operating SI engines on ammonia alone would not result in  
566 satisfactory combustion<sup>133</sup>. However, Starkman et al.<sup>126</sup> discovered that it is possible to  
567 achieve satisfactory combustion by using some type of combustion promoter. Common fuels  
568 used in ICEs such as gasoline and diesel, as well as alternative fuels like hydrogen, biodiesel,  
569 methanol can be used as combustion promoter<sup>138</sup>. Among them, hydrogen is considered the  
570 best promoter because it has characteristics that are opposite and supplement those of  
571 ammonia. Hydrogen possesses a rapid combustion rate, low ignition energy, and an extensive  
572 range of flammability<sup>139, 140</sup>. Research has demonstrated that adding even a small amount of  
573 hydrogen can significantly enhance the stability of ammonia combustion, resulting in more  
574 stable engine operation<sup>131, 141</sup>.

575 The experimental study of ammonia and hydrogen mixtures in SI engines is completely  
576 reported in<sup>134</sup>. Their results indicate that blends of ammonia and hydrogen are a viable fuel  
577 option for SI engines. The peak efficiency and IMEP were achieved when using a mixture  
578 encompassing 10% of hydrogen volume. The study of Sawyer et al.<sup>142</sup> found that 8% volume  
579 of hydrogen in the mixture was sufficient. Frigo and Gentili found that the minimum  
580 hydrogen to ammonia energy ratio to achieve the same engine behaviour as gasoline was 7%  
581 at full load and 11% at part load. Figure 14 shows the engine BTE with respect to the engine  
582 speed for ammonia – hydrogen combustion and for gasoline combustion at full load<sup>143</sup>.  
583 Furthermore, adding less than 10% H<sub>2</sub> to NH<sub>3</sub> (of the total mixture volume) ensured the  
584 combustion stability of the engine<sup>136</sup>. However, excessive hydrogen addition results in



585 decreasing ITE and IMEP of the engine as well as increasing NO<sub>x</sub> emissions due to the  
 586 formation of thermal NO<sub>x</sub><sup>141</sup>. Based on these experimental results, the optimal hydrogen  
 587 addition to ammonia is around 10%. Nevertheless, the hydrogen ratio may vary depending on  
 588 the specific engine design and operating conditions, and further research is needed to  
 589 determine the optimal hydrogen-to-ammonia ratio for different engine configurations.



590  
 591 Figure 14. Comparison of engine brake thermal efficiency (EBTE) versus engine speed with NH<sub>3</sub> – H<sub>2</sub>  
 592 and with gasoline at full load (License no: 5619241458175, reproduced from ref.<sup>143</sup>)

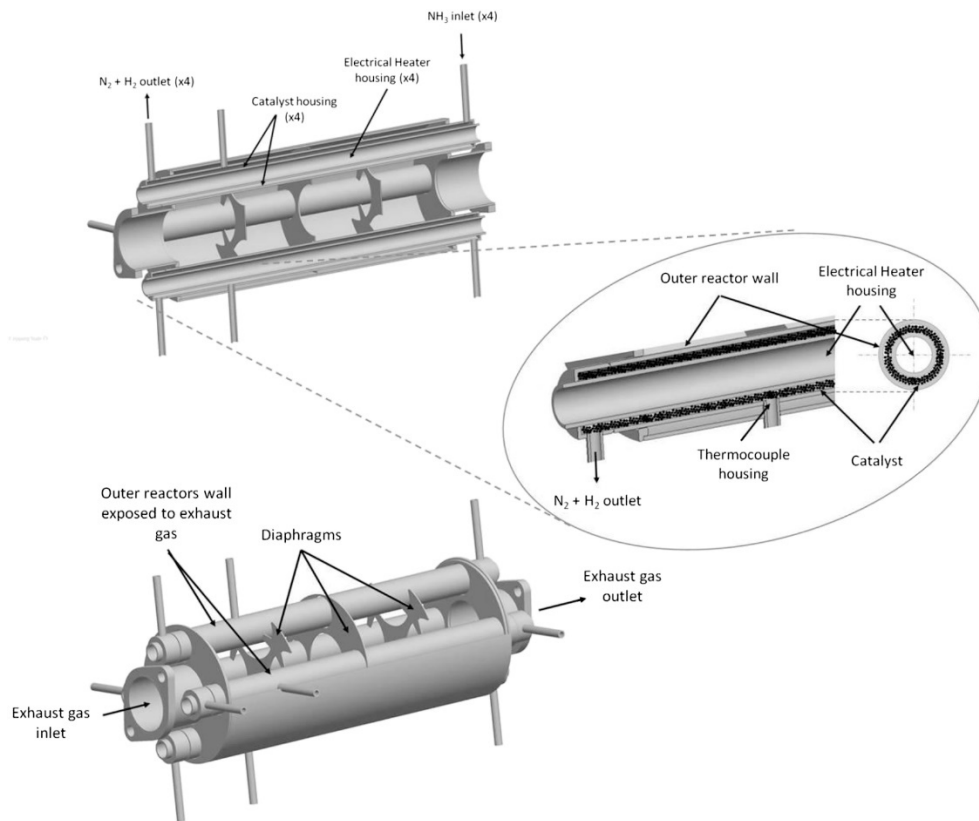
593 Furthermore, optimal performance of an engine operating on ammonia and hydrogen mixture  
 594 is achieved with an excess air ratio around stoichiometry and MBT timing, resulting in high  
 595 ITE and mean effective pressure<sup>134, 141</sup>. It has been found that operating near stoichiometric  
 596 conditions results in lower nitric oxide emissions than in hydrocarbon combustion. However,  
 597 the ammonia slip level is high (in the range of 1000 ppm) under these condition<sup>134</sup>. The  
 598 amount of ammonia slip from the engine may seem like a concern; it can actually be  
 599 beneficial in reducing NO<sub>x</sub> emissions by optimising the selective catalytic reduction (SCR)  
 600 catalyst<sup>144</sup>. Also, the ammonia slip level is dependent on CR rather than excess air ratio and  
 601 ignition timing, which is in contradiction to hydrocarbon-fuelled combustion engine.

### 602 3.2.3. Ammonia as a hydrogen carrier

603 One of the main problems with hydrogen is its low density, high storage pressure and the  
604 difficulty of storing it on board a vehicle. To address these challenges, ammonia can be used  
605 as a carrier for storage and transportation of hydrogen. By facilitating this hydrogen is  
606 extracted from the ammonia using a catalyst, and then used as fuel<sup>145, 146</sup>. This approach can  
607 provide an efficient and clean energy source while utilising existing infrastructure for  
608 ammonia production and distribution. Moreover, using ammonia as a hydrogen carrier can  
609 enable the use of dual-fuel engines that can run on both ammonia and hydrogen, providing  
610 flexibility and redundancy in the fuel supply<sup>140, 144, 147</sup>.

611 There are several onboard technologies that can be utilised to convert  $\text{NH}_3$  into  $\text{H}_2$ . One  
612 approach is the use of an ammonia decomposition reactor, which typically contains a metal  
613 catalyst such as ruthenium or nickel<sup>148</sup>. Another approach is the utilisation of an ammonia  
614 reformer, where ammonia is mixed with air or oxygen and passed over a catalyst, which  
615 promotes partial oxidation and steam reforming reactions to produce  $\text{H}_2$  and  $\text{N}_2$ <sup>149</sup>.

616 Simulation results of a hydrogen reforming system showed an increase in the peak value of  
617 in-cylinder pressure and heat release rate with an increase in  $\text{H}_2$  enrichment. The maximum  
618 ITE of 44.3% was achieved at  $\lambda = 1.2$  and 12.5% hydrogen addition<sup>150</sup>. Also, experimental  
619 results of a hydrogen generation system (illustrated in Figure 15), which uses a cracking  
620 reactor with a ruthenium-based catalyst in an  $\text{NH}_3/\text{H}_2$  engine, showed a trend in BTE and  
621 brake power similar to that of a gasoline engine. However, due to the poor mixture heating  
622 value, engine power output is reduced by 10% at low engine speed and 25% at high speed  
623 compared to gasoline engine's power output. Additionally, the only significant pollutant  
624 detected from the ammonia/hydrogen engine exhaust emissions was  $\text{NO}_x$ , with a peak value  
625 of 1700 ppm at 3000 rpm under full load conditions and 1500 ppm under low load<sup>143, 147</sup>.



626

627 Figure 15. Design and illustration of the catalytic cracker reactor and integrated heat exchangers for  
 628 hydrogen generation system (License no: 5619250191091, reproduced from ref.<sup>147</sup>)

629 Cold start is a challenge for ammonia engines because the chemical reactions required to  
 630 convert ammonia to hydrogen are only effective within a certain range of temperature range.  
 631 Currently, commercially catalysts must be heated to a temperature of 450°C or above to  
 632 facilitate the dissociation of ammonia into its constituent elements, nitrogen and hydrogen.  
 633 Therefore, during cold start, a higher hydrogen flow rate and engine speed are required and  
 634 maintained for a few seconds. Then, the H<sub>2</sub>/NH<sub>3</sub> ratio and engine speed is gradually reduced  
 635 to reach the controlled operating condition<sup>143</sup>. Autothermal reforming is reported to be  
 636 suitable for engine's cold-start performance in ammonia combustion. During the warm-up  
 637 process NH<sub>3</sub>-free emissions were obtained using a Cu-zeolite catalyst for adsorption. The  
 638 ratio of air to NH<sub>3</sub> introduced into the reformer was identified as a crucial factor in  
 639 controlling the proportion of H<sub>2</sub> in the fuel. Moreover, the combustion of an ammonia engine

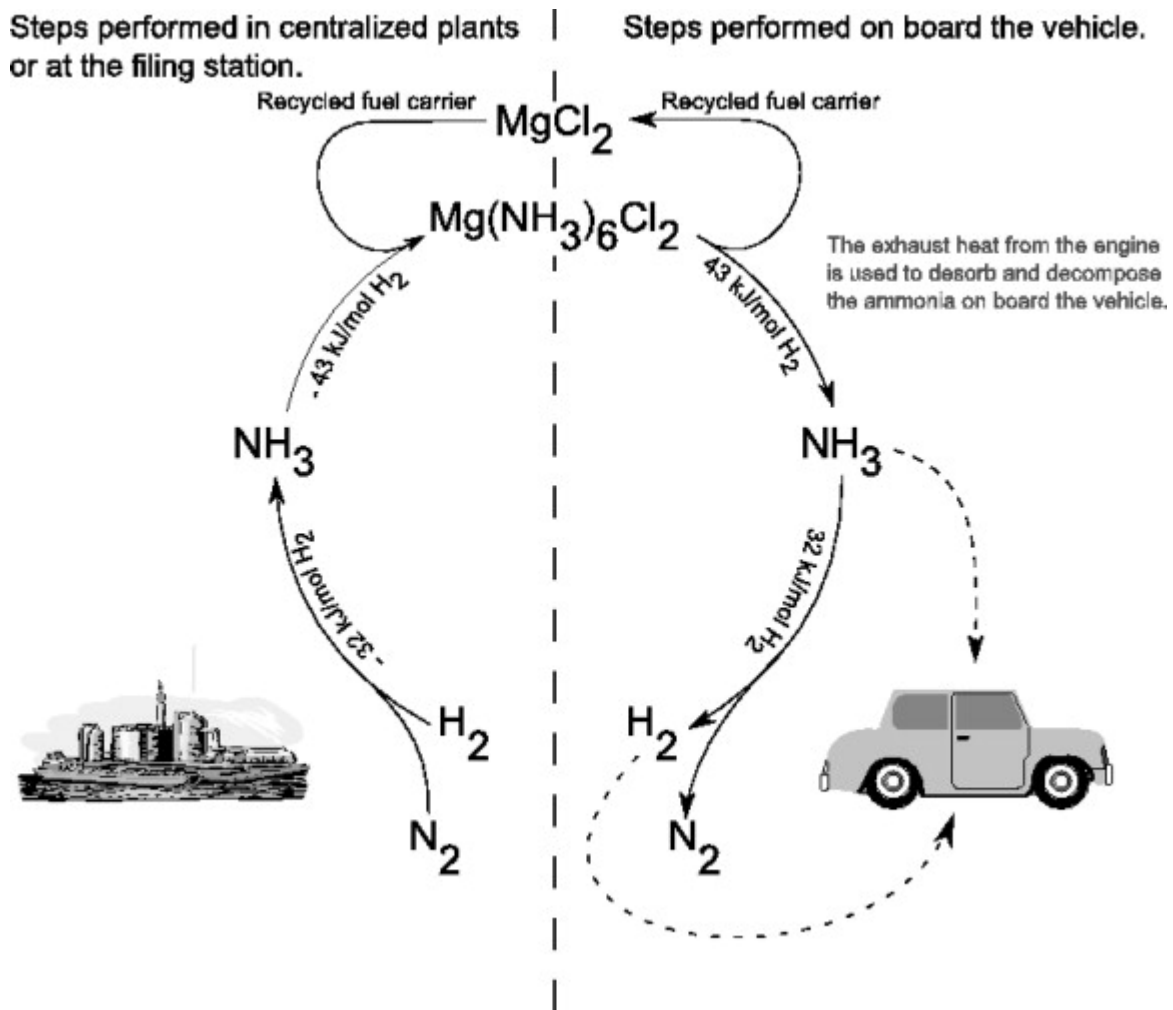
640 could be initiated with a mixture containing H<sub>2</sub>-NH<sub>3</sub> ratio of less than 10%. Additionally, a  
641 stable fast-idle combustion could be achieved by using a hydrogen to ammonia ratio of  
642 around 2:1 by volume<sup>151</sup>.

### 643 **3.3. Challenges with ammonia**

644 While ammonia is a promising fuel for LDVs, there are still several challenges that need to  
645 be addressed before it can become a mainstream fuel. One of the main challenges is the high  
646 cost of ammonia production. Currently, the most common method of producing ammonia is  
647 the Haber-Bosch process, which is energy-intensive and conventionally relies heavily on  
648 fossil fuels. In order for ammonia to be considered as a green fuel, production must shift  
649 towards renewable energy sources.

650 Another challenge is the infrastructure needed to support ammonia fuelling stations.  
651 Currently, there are very few ammonia fuelling stations, and building a new infrastructure  
652 network would require significant investment. Additionally, ammonia is highly toxic and  
653 requires special safety measures when handling and storing it.

654 Furthermore, ammonia has a lower energy density than gasoline or diesel fuel, which means  
655 that it requires larger fuel tanks to provide the same driving range. This could limit the  
656 amount of space available for passengers or cargo in LDVs. One possible method for storing  
657 ammonia is a metal amine complex system (Mg(NH<sub>3</sub>)<sub>6</sub>Cl<sub>2</sub>)<sup>152</sup>. Figure 16 shows a potential  
658 configuration for a fuel system utilising the metal amine complex as a carrier for ammonia.  
659 Due to the high exhaust gas temperature it becomes feasible to fulfill a significant portion of  
660 the heat required for extracting ammonia and hydrogen from a metal amine complex, through  
661 the use of residual heat in the exhaust gas<sup>134</sup>.



662

663 Figure 16. Method of using metal amine complex system ( $Mg(NH_3)_6Cl_2$ ) as ammonia/hydrogen  
 664 carrier in light-duty vehicles (License no: 5619250329448, reproduced from ref.<sup>134</sup>)

665 In addition, the efficiency of the ammonia-based fuel system needs to be improved. One  
 666 approach is to develop more efficient catalysts that can convert ammonia into hydrogen at  
 667 lower temperatures. Another approach is to operate ammonia in combination with other fuels,  
 668 such as hydrogen to increase the overall energy density of the fuel. Also, due to the slower  
 669 combustion rate of ammonia, this can result in slower acceleration and a reduced maximum  
 670 speed, which can be a significant drawback for certain applications. Various strategies such  
 671 as improving the combustion process by using more efficient combustion technologies,  
 672 optimising the engine design, and developing new ammonia-based fuels with higher energy  
 673 densities could be used. Nevertheless, there exists a scarcity of data concerning the

674 performance of vehicles fuelled by ammonia, and further research is imperative to  
675 comprehensively grasp their capabilities and constraints.

676 Another challenge associated with ammonia as a fuel is the design of the fuel injector.  
677 Currently there are no ammonia injectors available on the market. Furthermore, ammonia is  
678 corrosive to certain materials, which can limit the choice of materials that can be used in the  
679 injector and other fuel system components. As a result, there is a need for research and  
680 development of fuel injectors that are optimised for ammonia fuel, with improved  
681 atomisation and mixing capabilities, and that can withstand the harsh conditions associated  
682 with ammonia combustion.

683 Finally, there are concerns about the emissions of nitrogen oxides (NO<sub>x</sub>) from ammonia-  
684 fuelled vehicles. While ammonia can be acted as a reductant for SCR in diesel-powered  
685 engines, in SI engines ammonia combustion can lead to higher NO<sub>x</sub> emissions. This is  
686 because of the nitrogen content in the ammonia molecule and high combustion temperature  
687 which prompts NO<sub>x</sub> formation. Also, thermal NO<sub>x</sub> formation is the primary mechanism for  
688 NO<sub>x</sub> formation in ammonia combustion. At high temperatures N<sub>2</sub> and O<sub>2</sub> react to form NO  
689 through the Zeldovich mechanism. The presence of oxygen in the combustion process further  
690 promotes the conversion of NO to NO<sub>2</sub>. One approach to reducing NO<sub>x</sub> emissions is to use  
691 EGR and lean combustion, which can reduce the combustion temperature and reduce the  
692 formation of NO<sub>x</sub>. Additionally, SCR systems can be used to reduce NO<sub>x</sub> emissions by  
693 converting NO<sub>x</sub> into nitrogen and water vapor, these could use NH<sub>3</sub> as the reductant agent.  
694 However, more in-depth research is needed to optimise the use of ammonia as a fuel and to  
695 develop new technologies to further reduce emissions.

#### 696 **4. Techno-economics analysis**

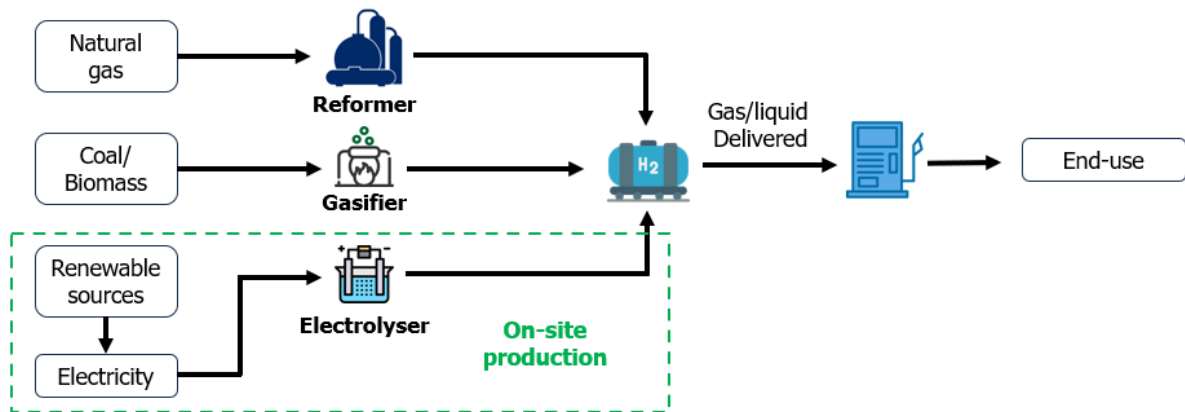
697 From the results above, it can be seen that hydrogen and ammonia are potential alternative  
698 fuels for LDVs, that could contribute to a carbon free mobility future. However, a  
699 comprehensive assessment of their viability and adoption necessitates an exploration of the  
700 entire value chain from production to end-use. Key factors include the technical limitation,  
701 economy impacts such as capital and operating costs of production through various primary  
702 energy sources and processes, delivery and distribution infrastructure requirements,  
703 utilisation technologies and associated costs, as well as the value proposition and  
704 competitiveness in LDVs applications. Additionally, understanding the potential risks  
705 associated with hydrogen and ammonia fuels is crucial for scaling up and realise its  
706 widespread application.

##### 707 *Technical limitation:*

708 Given the technical feasibility of hydrogen and ammonia fueled LDVs is well-established,  
709 infrastructure development is needed to allow its benefits. Figure 17 illustrates the general  
710 hydrogen pathways of hydrogen supply chain, it can be categorised by the production sources  
711 (e.g. natural gas, biomass, water electrolysis) or by distribution method like delivered or on-  
712 site production via renewable electricity. However, the technology and status of deployment  
713 hydrogen infrastructure have lagged behind<sup>153</sup>. Hydrogen produced through various methods  
714 contributes to a cleaner and more sustainable production process. Moreover, hydrogen  
715 storage and transportation technologies have seen considerable progressed, addressing  
716 challenges related to density and safety<sup>154</sup>.

717 To overcome the challenge of low density associated with hydrogen, ammonia can be served  
718 as a carrier for hydrogen storage and transportation. Using ammonia as the sole fuel onboard  
719 allows for higher energy density without requiring cryogenic temperatures or pressure. The

720 Haber-Bosch process, traditionally used for ammonia production, is well-established.  
 721 Furthermore, ongoing research explores advanced methods, including green ammonia  
 722 production through electrochemical synthesis and biological processes. Also, studies have  
 723 proposed using ammonia as the only onboard fuel stream, avoiding the need for complex fuel  
 724 distribution infrastructure of two fuels<sup>134, 152</sup>.



725  
 726 Figure 17. General hydrogen distribution pathways.

727 *Economic feasibility:*

728 Commercialisation of hydrogen vehicles faces challenges due to high costs of building  
 729 hydrogen stations. However, the average capital costs of for hydrogen stations have  
 730 significantly decreased, from over \$20,000 per kg daily capacity in 2009 to ~\$5000 per kg  
 731 daily capacity in 2015, and further to approximately \$1,200 and \$3,000 per kilogram of  
 732 hydrogen dispensed per day<sup>155</sup>. This reduction is attributed to the development of hydrogen  
 733 production methods and decreasing costs of renewable energy sources, such as solar and  
 734 wind, contributing to the economic viability of hydrogen production. Additionally,  
 735 advancements in electrolysis and other production methods aim to enhance the  
 736 competitiveness of hydrogen with conventional fuels. In contrast, ammonia production  
 737 currently relies on traditional Haber-Bosch process which is energy-intensive and require  
 738 fossil fuels. Green ammonia production methods, utilising renewable energy, aim to enhance



739 economic viability. When produced on a large scale, ammonia might replace a significant  
740 portion of today's liquid fuel usage.

741 *Competitiveness with fossil fuel:*

742 While the performance of H2ICE LDVs can be comparable with traditional vehicles,  
743 hydrogen faces competition from traditional fossil fuels due to the cost parity with fossil  
744 fuels. Currently the cost of hydrogen is about \$10 – \$16 per gge (where the energy of 1 kg of  
745 hydrogen is approximately equivalent to the energy of one gallon of gasoline). This is  
746 significantly higher than the target competitive price for alternative fuels, which is \$5/gge<sup>156</sup>.  
747 However, studies have reported that the cost of hydrogen fuel could be competitive with  
748 traditional fuel such as gasoline or diesel by reducing infrastructure-related costs<sup>157</sup>.

749 On a source-to-tank basis, a study by Wright et al.<sup>158</sup> indicates that the manufacturing cost of  
750 hydrogen could be about \$6.55 per gge. In the same scenario, ammonia costs \$4.50 per gge,  
751 representing a 31% cost advantage over hydrogen, highlights a clear economic advantage of  
752 ammonia. However, for a comprehensive assessment, the efficiency of the power source and  
753 drivetrain should be considered to provide per-km costs. Assuming a hydrogen vehicle fuel  
754 efficiency of 90 km per gge the hydrogen fuel cost is \$0.072 per km while ammonia is \$0.075  
755 per km<sup>159</sup>. Ammonia's perceived higher cost in the model is influenced by the assumed lower  
756 efficiency, impacting its overall economic comparison with hydrogen.

757 *Market analysis:*

758 The market for both hydrogen and ammonia is expanding rapidly, driven by a growing  
759 interest in decarbonisation. Industries such as transportation, manufacturing, and energy are  
760 increasingly adopting these fuels as cleaner alternatives to fossil fuel. The widespread  
761 adoption of hydrogen fueled vehicle technology in zero-carbon mobility are directly linked to  
762 the advancement and cost reduction of hydrogen technology. Furthermore, scaling up the  
763 production and charging stations is a critical aspect of the widespread adoption of these

764 vehicles. Investments in large-scale production facilities and infrastructure are essential<sup>160</sup>.  
765 While ammonia offer more advantages such as less space is required for the same energy  
766 content and having more competitive on current market prices, scaling up ammonia  
767 production involves addressing challenges related to energy efficiency and environmental  
768 impact<sup>161</sup>.

#### 769 *Risk Analysis:*

770 While the potential benefits of hydrogen are substantial, there are inherent risks, including  
771 technological challenges, market uncertainties, and regulatory changes. The investment  
772 required for infrastructure development poses financial risks. Additionally, ensuring safety in  
773 hydrogen production, storage, and transportation is a key consideration. Due to hydrogen is  
774 being easy to leak and diffuse, which is difficult to detect after leakage, it can accumulate in  
775 confined spaces, posing a potential threat of fire and explosion accidents. However, the  
776 number of literatures on hydrogen vehicles safety is limited. From the hydrogen stations  
777 aspect, majority of the public safety reports involve minor leakage, demonstrating an  
778 excellent safety record<sup>157</sup>.

779 In terms of safety, ammonia is not flammable in the air and is therefore less likely to cause  
780 fires and explosions. The primary concern with ammonia is its toxicity, which poses risks to  
781 human health. Accidental releases or exposure incidents must be carefully managed to  
782 prevent adverse health effects and widespread public adoption.

### 783 **5. Concluding remarks**

784 Overall, zero-carbon fuels such as hydrogen and ammonia have the potential to play a crucial  
785 role in achieving sustainable mobility and reducing carbon emissions. While each fuel type  
786 presents its unique advantages and challenges, continued research and development will be  
787 necessary to improve their feasibility and realise a zero-carbon economy. While hydrogen

788 offers high energy density and zero carbon emissions, it presents challenges in storage,  
789 transportation, and infrastructure development. Ammonia, on the other hand, can be stored  
790 and transported more easily but has lower energy density and poses challenges in emissions  
791 reduction and overall engine performance.

792 In addition, there is also the possibility of using combinations of ammonia and hydrogen in  
793 an engine. This approach can potentially provide the benefits of both fuels while mitigating  
794 their individual drawbacks. For example, using ammonia as the primary fuel and hydrogen as  
795 the secondary fuel can help to overcome some of the challenges associated with using  
796 ammonia as a standalone fuel, such as high NO<sub>x</sub> emissions and a limited performance  
797 envelope by speeding up the flame front propagation and stabilising the combustion.  
798 However, further research and development is needed to optimise the use of ammonia and  
799 hydrogen as dual fuels in light-duty vehicles. This includes investigating the most effective  
800 fuel injection strategies, combustion control, and emissions control technologies.

801 Clearly, the environmental benefits of using ammonia and hydrogen as fuel in LDVs are only  
802 fully realised if these fuels are derived from renewable sources. While both ammonia and  
803 hydrogen hold the promise of reducing greenhouse gas emissions and improve air quality,  
804 their production from fossil fuels may actually increase emissions and exacerbate climate  
805 change. Therefore, it is essential to prioritise the advancement of renewable sources based  
806 methods for producing ammonia and hydrogen, such as through electrolysis using renewable  
807 electricity or biomass gasification. This not only makes their use in transportation more  
808 sustainable but also ensures that the overall energy system is decarbonised.

809 In addition to renewable production, there is also a need to address the technical and  
810 infrastructural challenges associated with their use as fuel sources in LDVs. Furthermore,  
811 safety concerns will arise when using hydrogen and ammonia as fuel in LDVs. Hydrogen is a  
812 highly flammable gas and storing it at high pressures can increase the risk of explosions and

813 fires in the event of a collision or leak. Proper safety measures, such as reinforced fuel tanks  
814 and advance storage technology must be implemented to prevent accident ignition and ensure  
815 public safety. Similarly, ammonia is a toxic gas that can cause serious harm if inhaled or  
816 exposed to the skin or eyes. Special care must be taken during the handling, transport, and  
817 storage of ammonia to prevent leaks or spills that could endanger public health and the  
818 environment.

819 Overall, the use of ammonia and hydrogen as alternative fuel sources in LDVs has significant  
820 potential to contribute to a more sustainable and decarbonised transportation sector.  
821 However, their full potential can only be realised through a comprehensive approach that  
822 includes renewable production, technical development, and infrastructure deployment, as  
823 well as must consideration of the safety aspect associated with the gases.

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1305 **Abbreviations**

BEV	Battery electric vehicles
BTE	Break thermal efficiency
CFR	Cooperative fuel research
CR	Compression ratio
DI	Direct injection
EGR	Exhaust gas recirculation
GDI	Gasoline direct injection
GHG	Greenhouse gas
H2ICE	Hydrogen internal combustion engine
HC	Hydrocarbon
ICE	Internal combustion engines
IMEP	Indicated mean effective pressure
ITE	Indicated thermal efficiency
LDV	Light-duty vehicle
NA	Naturally aspirated
PFI	Port fuel injection
SCR	Selective catalytic reduction
SI	Spark ignition
VCR	Variable compression ratio

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