Ammonia as hydrogen carrier for transportation; investigation of the ammonia exhaust gas fuel reforming
Wang, Wentao; Herreros, José M.; Tsolakis, Athanasios; York, Andrew P.e.

DOI:
10.1016/j.ijhydene.2013.05.144

License:
Creative Commons: Attribution (CC BY)

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):

Link to publication on Research at Birmingham portal

Publisher Rights Statement:
Eligibility for repository: checked 02/04/2014

General rights
Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

• Users may freely distribute the URL that is used to identify this publication.
• Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
• Users may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
• Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy
While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.
Ammonia as hydrogen carrier for transportation; investigation of the ammonia exhaust gas fuel reforming☆

Wentao Wang a, José M. Herreros a, Athanasios Tsolakis a,*, Andrew P.E. York b

a School of Mechanical Engineering, University of Birmingham, Edgbaston B15 2TT, UK
b Johnson Matthey Technology Centre, Blount’s Court, Sonning Common, Reading RG4 9NH, UK

ARTICLE INFO

Article history:
Received 25 March 2013
Received in revised form
21 May 2013
Accepted 26 May 2013
Available online 24 June 2013

Keywords:
Ammonia
Hydrogen
Reforming
Diesel
Emissions

ABSTRACT

In this paper we show, for the first time, the feasibility of ammonia exhaust gas reforming as a strategy for hydrogen production used in transportation. The application of the reforming process and the impact of the product on diesel combustion and emissions were evaluated. The research was started with an initial study of ammonia autothermal reforming (NH3–ATR) that combined selective oxidation of ammonia (into nitrogen and water) and ammonia thermal decomposition over a ruthenium catalyst using air as the oxygen source. The air was later replaced by real diesel engine exhaust gas to provide the oxygen needed for the exothermic reactions to raise the temperature and promote the NH3 decomposition. The main parameters varied in the reforming experiments are O2/NH3 ratios, NH3 concentration in feed gas and gas hourly space velocity (GHSV). The O2/NH3 ratio and NH3 concentration were the key factors that dominated both the hydrogen production and the reforming process efficiencies: by applying an O2/NH3 ratio ranged from 0.04 to 0.175, 2.5–3.2 l/min of gaseous H2 production was achieved using a fixed NH3 feed flow of 3 l/min. The reforming reactor products at different concentrations (H2 and unconverted NH3) were then added into a diesel engine intake. The addition of considerably small amount of carbon–free reformate, i.e. represented by 5% of primary diesel replacement, reduced quite effectively the engine carbon emissions including CO2, CO and total hydrocarbons.

1. Introduction

The use of hydrogen in internal combustion engines has long been believed to be beneficial in terms of emissions reduction such as HCs, CO, CO2 and particulate emissions [1,2]. Additionally, its utilisation has been proven to be effective in enhancing automotive aftertreatment performance especially at low engine exhaust gas temperatures [3,4]. However, its low volumetric energy density and its high transportation cost make on-board hydrogen storage difficult [5]. Previous studies have shown that H2 can be produced by means of hydrocarbon reforming [6,7]. This method can be also adopted for the purpose of on-board reforming of hydrocarbon fuel i.e., using recovered heat and oxidant from exhaust gases for...
driving fuel reforming. This is considered as a potential solution to deal with the hydrogen storage issue [8]. Recently, increasing numbers of studies have shown that hydrogen production can be implemented through ammonia thermal decomposition for small scale fuel cell power systems [9-12]. Decomposition of ammonia is by definition COx free, and CO2 yielded during ammonia synthesis can be sequestrated onsite at the production plants [13-15]. Thus using ammonia as a hydrogen source is potentially an alternative to the conventional hydrocarbon reforming and makes the on-board hydrogen production free of COx.

Ammonia has been overlooked in the past for vehicular applications; both as a fuel and a hydrogen carrier. In general, its low heating value on mass basis indicates ammonia has less energy for combustion than conventional fossil fuels i.e. gasoline and diesel. However, the stoichiometric air - fuel ratio for ammonia is much lower compared to diesel fuel. This results in ammonia having an LHV of 2.64 MJ per kg of stoichiometric mixture, which is comparable to that of diesel (2.77 MJ/kg) [16]. Nonetheless, because of ammonia’s relatively high auto-ignition temperature (651 °C) compared to 254 °C for diesel), complete in-cylinder combustion of ammonia is difficult, which leads to significant emission of NH3 [17]. It should be noticed that 1 mol of ammonia contains 1.5 mol of hydrogen, which is 17.8% by weight or 108 kg – H2/m3 embedded in liquid ammonia at 20 °C. Comparing this to the most advanced hydrogen storage systems, e.g. metal hydrides, which store H2 up to 25 kg/m3, the advantage of ammonia in carrying hydrogen per unit volume is significant [18]. Therefore, using hydrogen extracted from ammonia appears to be more beneficial than combusting ammonia directly in an IC engine. Zamfirescu [13] in a recent study compared NH3 with other common fuels such as gasoline, CNG, LPG and methanol, showing that NH3 is competitive to these fuels in terms of gravimetric, volumetric and energetic costs (see in Table 1). Based on this study, a further comparison between each fuel’s molar hydrogen carrying ability per unit mass, volume and cost can be made, which indicates ammonia is a more affordable hydrogen carrier, Table 2.

In addition to that, the storage, distribution and transportation infrastructure of ammonia is established [19], with 100 million tonnes of ammonia being delivered each year. Thus the existing production and handling system of ammonia reveal a great potential in expanding its usage to vehicle applications as a sustainable fuel [20]. Ammonia has already been applied but in the form of urea on today’s heavy duty diesel vehicles for catalytic aftertreatment systems for NOx reduction. Therefore special technology and regulation for safe storage of ammonia on passenger cars should be developed or an additional step of thermo-catalytic conversion of urea to ammonia should be applied as shown in the literature [21].

As reported in earlier studies, a temperature higher than 500 °C is required for catalytic NH3 decomposition in order to achieve stable NH3 conversion and high H2 production [5,22-24]. However, for on-board applications the exhaust gas temperature of a typical diesel engine is only in the range of 150-400 °C. Thus a mechanism is required to raise the temperature of the gas stream for the purpose of on-board NH3 decomposition. The new approach is to apply the same principle as that of autothermal reforming (ATR) and exhaust gas fuel reforming, where part of the fuel is oxidised to provide the energy needed by a subsequent fuel reforming mechanism to produce H2. If sufficient ammonia oxidation takes place, the endothermic ammonia decomposition can be self - sustaining using the provided heat.

The expected selective catalytic oxidation of ammonia (into nitrogen and water) and NH3 decomposition reactions are expressed by Eqs. (1) and (2), respectively. The desired combination is shown by Eq. (3).

\[4NH_3 + 3O_2 = 6H_2O + 2N_2; \Delta H = -1260kJ/mol\]  
\[2NH_3 = 3H_2 + N_2; \Delta H = +46kJ/mol\]  
\[NH_3 + xO_2 = 2xH_2O + (1.5 - 2x)H_2 + 0.5N_2; x < 0.75\]

In Eq. (3), x represents the O2/NH3 molar ratio, a parameter which controls the intensity of the exothermic portion in the overall process, which can in turn determine the stoichiometric yield of hydrogen. In the current study, air is used to provide the oxygen needed by the reaction and is referred NH3 – ATR throughout. Furthermore, if diesel engine exhaust is used to provide the O2, and part of the exhaust heat is recovered as a primary energy source for the reaction then the NH3 – ATR is transformed into NH3 exhaust gas reforming.

To summarise, in this research, three different experiments were performed and analysed. Firstly, the catalytic NH3 decomposition was studied at different temperatures. Secondly, the oxidative mechanism of ammonia and NH3 decomposition were combined enabling NH3 – ATR and NH3 exhaust

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline, C8H18/liquid</td>
<td>1</td>
<td>736</td>
<td>46.7</td>
<td>34.4</td>
<td>1.36</td>
<td>1000</td>
<td>29.1</td>
</tr>
<tr>
<td>CNG, CH4/integrated storage</td>
<td>250</td>
<td>188</td>
<td>42.5</td>
<td>10.4</td>
<td>1.20</td>
<td>226</td>
<td>28.2</td>
</tr>
<tr>
<td>LPG, C3H8/pressurised tank</td>
<td>14</td>
<td>388</td>
<td>48.9</td>
<td>19.0</td>
<td>1.41</td>
<td>548</td>
<td>28.8</td>
</tr>
<tr>
<td>Methanol, CH4OH/liquid</td>
<td>1</td>
<td>786</td>
<td>14.3</td>
<td>11.2</td>
<td>0.54</td>
<td>421</td>
<td>37.5</td>
</tr>
<tr>
<td>Hydrogen, H2/metal hydrides</td>
<td>14</td>
<td>25</td>
<td>142.0</td>
<td>3.60</td>
<td>4.00</td>
<td>100</td>
<td>28.2</td>
</tr>
<tr>
<td>Ammonia, NH3/pressurised tank</td>
<td>10</td>
<td>603</td>
<td>22.5</td>
<td>13.6</td>
<td>0.30</td>
<td>181</td>
<td>13.3</td>
</tr>
</tbody>
</table>

HHV: higher heating value per kg, HHV: higher heating value per m³, c: cost per kg, C: cost per m³.
gas reforming. Finally, the yielded reformate (H₂ and unconverted NH₃) was sent back to a diesel engine to examine how a reforming system affects the combustion process and emissions.

2. Experimental and methodology

2.1. Catalyst

In this study, a ruthenium catalyst was chosen, given its activity in both ammonia oxidation [25] and decomposition [22,26]. The catalyst was provided by Johnson Matthey and coated on 1/8 inch OD γ-Al₂O₃ pellet supports with a loading ratio of 2% by weight.

2.2. Test setup

All reforming tests were carried out in a laboratory reforming reactor, which is shown in Fig. 1. The catalyst was loaded inside a stainless steel reactor (15 mm in diameter) that was held vertically within a tube furnace. At the centre of the catalyst bed, a tubular sheath was fitted, which was made from a stainless steel tube with one end sealed. In order to investigate the process’s thermal behaviour, a k-type thermocouple was inserted into the sheath to record the reaction temperature along the catalyst bed. Ammonia was supplied by a gas bottle and injected into the reactor, controlled by a flow metre. Nitrogen and air were introduced at separate inlets of the reactor. Before each experiment, inert nitrogen was initially introduced through the reactor to make sure the temperature gradient along the catalyst bed was minimised. For ammonia exhaust gas reforming part of the diesel engine exhaust was extracted from the exhaust manifold and was introduced into the reactor. The exhaust flow rate was controlled to meet different O₂/NH₃ ratios. NH₃ flow at varying O₂/NH₃ ratios and NH₃ concentrations (Table 3). Following that NH₃ + ATR was sent back to a diesel engine to examine how a reforming system affects the combustion process and emissions.

2.4. Reforming process efficiency

The process efficiency η was defined as the lower combustion enthalpy rate (kJ/sec) of the product stream divided by the lower combustion enthalpy rate (kJ/sec) of the reactant stream. Here, the product stream can be either defined as the produced H₂ alone or H₂ combined with any unconverted NH₃ (both can be considered as fuels to the engine). Thus two efficiencies, namely hydrogen efficiency and reforming process efficiency can be adopted to evaluate the reforming performance. These are defined by Eqs. (4) and (5) below:

\[ \eta_h(\%) = \frac{LCV_{H2} \times m_{H2}}{LCV_{NH3} \times m_{NH3}} \times 100\% \] (4)  

\[ \eta_{of}(\%) = \frac{(LCV_{H2} \times m_{H2}) + (LCV_{NH3} \times m_{NH3})}{LCV_{NH3} \times m_{NH3}} \times 100\% \] (5)

where LCVₜₜ, and LCVₜₜ, are the lower calorific values of the produced H₂ and the gas feed NH₃, whereas mₜₜ and mₜₜ are the mass flow rates of NH₃ and H₂ respectively.

3. Results and discussion

3.1. NH₃ decomposition over Ru – Al₂O₃ catalyst

3.1.1. Temperature effect

Fig. 2(a) depicts the decomposition of pure NH₃ at different reactor inlet temperatures. In addition to experimental results, an equilibrium calculation for NH₃ decomposition was made using an STANJAN equilibrium model (v 3.91, Stanford University) at the same temperatures as those of the
experimental studies. As predicted by the equilibrium simulation, increased temperature leads to increased NH₃ conversion due to enhanced decomposition kinetics and rate [27]. 100% conversion without catalytic promotion is calculated for temperatures as low as 300 °C. However, when the non-catalytic decomposition was experimentally performed over the plain γ-Al₂O₃ pellet support, no significant NH₃ conversion was observed until the reactor inlet temperature reached 500 °C. The same discrepancy was observed in literature [22] and [28], which implies the equilibrium of non-catalytic NH₃ decomposition was hard to achieve at lower reaction temperatures. Hence, catalytic assistance must be adopted for easier activation: in the presence of ruthenium catalyst, the NH₃ decomposition light off temperature was reduced to 300 °C in the current study, and NH₃ conversion was higher, than with only alumina, across the whole temperature range.

From the results presented, it is clear that to achieve NH₃ decomposition in the relatively low temperature range applicable to diesel exhaust i.e. 150–400 °C, the decomposition needs to be accompanied by an exothermic reaction. Therefore, adding an oxygen containing flow (air or exhaust) into the reactor is needed to promote the desired autothermal reaction, i.e. Eq. (3). This results in a variation in GHSV (increased total flow), and in diluted NH₃ feed (NH₃ mixed with oxygen containing flow). Thus prior to the NH₃ – ATR and NH₃ exhaust gas reforming, both GHSV and NH₃ inlet concentration were varied separately to study their impacts on the catalyst activity.

### 3.1.2. GHSV effect

As shown by Fig. 2(b), when the catalyst inlet temperature was fixed at 800 °C, increasing GHSV decreased the ammonia conversion from around 95% at 18000 h⁻¹–75% at 36000 h⁻¹.

### Table 3 – Test conditions for NH₃ decomposition.

<table>
<thead>
<tr>
<th></th>
<th>NH₃ (l/min)</th>
<th>N₂ (l/min)</th>
<th>Total flow (l/min)</th>
<th>NH₃ (%)</th>
<th>Cat. inlet temp (°C)</th>
<th>GHSV (h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature effect</td>
<td>2</td>
<td>–</td>
<td>2</td>
<td>100</td>
<td>300–800</td>
<td>18000</td>
</tr>
<tr>
<td>GHSV effect</td>
<td>2–4</td>
<td>–</td>
<td>2–4</td>
<td>100</td>
<td>800</td>
<td>18000–36000</td>
</tr>
<tr>
<td>NH₃ Conc. effect</td>
<td>2–4</td>
<td>0–2</td>
<td>4</td>
<td>50–100</td>
<td>300–800</td>
<td>36000</td>
</tr>
</tbody>
</table>

Fig. 1 – Schematic diagram of the test setup.
This is due to reduced residence time of the NH₃ over the catalyst at the region where the endothermic reaction is active (i.e. will be described in 3.2 sections) resulting in lowered decomposition efficiencies [29].

### 3.1.3. NH₃ concentration effect

Fig. 2(c) illustrates the ammonia conversion as a function of temperature and ammonia concentration in the feed gas. Instead of using pure NH₃, nitrogen was co-fed into the reactant stream. The total inlet flow was kept constant at 4 l/min, resulting in a GHSV of 36000 h⁻¹. It is shown that as the inlet ammonia concentration reduced, the NH₃ conversion increased for a fixed temperature. In earlier studies, hydrogen was found to be inhibitive to NH₃ decomposition. This is because the NH₃ decomposition is limited by a chemical equilibrium between the forward and reverse reactions. A high H₂ partial pressure and a low reaction temperature will contribute to a retarded forward rate of the NH₃ decomposition [30–34]. This explains the shift of NH₃ conversion to higher temperatures as the ammonia concentration in the feed gas increased. When the NH₃ concentration is higher in a constant reactant flow, the amount of H₂ produced is higher and thus the inhibition is more pronounced [5]. The other product of the reaction, N₂, is seen to have negligible influence on the forward rate [5,30,32]. In the current study, nitrogen behaved mainly as an inert gas, which diluted the inlet NH₃ to lower concentrations. In this case, reactions with lower inlet NH₃ concentrations show similar conversions at lower temperatures as those with high concentrations of NH₃.

### 3.2. Combined NH₃ oxidation and decomposition: NH₃ – ATR and NH₃ exhaust gas reforming

#### 3.2.1. Temperature profiles

In Fig. 3(a) – (c), the thermal behaviour of the combined reaction (Eq. (3)) at different O₂/NH₃ ratios was reflected by the temperature profile along the catalyst bed. For both NH₃ – ATR and NH₃ exhaust gas reforming, the reactor temperature increased abruptly near the catalyst inlet and declined thereafter. The temperature rise at catalyst inlet was due to NH₃ oxidation (Eq. (1)); the decrease was associated with the endothermic ammonia decomposition (Eq. (2)) and the reactor heat losses [8]. Such observation is in agreement with previous researches [35,36], where mechanisms of exothermic and endothermic were combined and performed.

In general, by varying the O₂/NH₃ ratio from 0.04 to 0.175 in both NH₃ – ATR and exhaust gas reforming, the temperature increase along the catalyst bed was enhanced, meaning increased oxygen input promoted the exothermic reaction. In addition to that, the higher the O₂/NH₃ ratio, the larger the temperature drop in the endothermic area, indicating improved NH₃ decomposition along the catalyst bed (this will be confirmed by increased hydrogen formation shown in the next section).

For NH₃ – ATR (Fig. 3(a) and (b)), similar temperature increases were observed over the 8 g and 16 g catalyst beds. However, compared to the 8 g catalyst bed, the temperature decrease was found to be more pronounced at the 16 g catalyst at each tested O₂/NH₃ ratio. This is caused by the greatly increased residence time over the 16 g catalyst strengthening the NH₃ decomposition through a better use of the available enthalpy [29].

When NH₃ – exhaust mixtures were introduced into the 16 g catalyst, the rise in temperature profiles (Fig. 3(c)) were slightly weakened at each O₂/NH₃ condition compared to those for the tests with air. As the engine exhaust contains only 10–15% oxygen by volume, the flow of the exhaust required to maintain the same O₂/NH₃ ratio was increased from that of the air, and so was the GHSV (Table 4). The main diesel exhaust gas components (e.g. CO₂ and H₂O) are known as heat absorbers due to their relatively large specific heat capacities [37]. Therefore, the temperature decrease in the reactor could be associated with the heat absorption of those species.

#### 3.2.2. NH₃ conversion and H₂ production

The NH₃ conversion at different O₂/NH₃ ratio is depicted in Fig. 4(a) for NH₃ – ATR over the 8 g and 16 g catalysts. The

| Table 4 – Test conditions for NH₃ – ATR and NH₃ exhaust gas reforming. |
|---------------------------|---------------------------|---------------------------|
| O₂/NH₃                   | 8 g catalyst bed (NH₃ – ATR) | 16 g catalyst bed (NH₃ – ATR) | 16 g catalyst bed (NH₃ Exhst. Ref.) |
| Tot. Flow (l/min) (NH₃ + Air) | GHSV (h⁻¹) | NH₃ Conc. (%) | Tot. Flow (l/min) (NH₃ + Air) | GHSV (h⁻¹) | NH₃ Conc. (%) | Tot. Flow (l/min) (NH₃ + Exh) | GHSV (h⁻¹) | NH₃ Conc. (%) |
| 0.04                     | –                     | –                     | 3 + 0.67 | 13392 | 84                  | 3 + 0.79 | 14230 | 79.05        |
| 0.06                     | 3 + 0.86               | 28928 | 77.78                        | 3 + 0.86 | 14464 | 77.78                        | 3 + 1.19 | 15720 | 71.56        |
| 0.08                     | 3 + 1.14               | 31071 | 72.41                        | 3 + 1.14 | 15535 | 72.41                        | 3 + 1.58 | 17210 | 65.37        |
| 0.09                     | 3 + 1.29               | 32142 | 70.00                        | 3 + 1.29 | 16071 | 70.00                        | 3 + 1.78 | 17955 | 62.65        |
| 0.12                     | 3 + 1.71               | 35357 | 63.64                        | 3 + 1.71 | 17678 | 63.64                        | 3 + 2.38 | 20190 | 55.72        |
| 0.15                     | 3 + 2.14               | 38571 | 58.33                        | 3 + 2.14 | 19285 | 58.33                        | 3 + 2.98 | 22425 | 50.16        |
| 0.175                    | 3 + 2.50               | 41250 | 54.55                        | 3 + 2.50 | 20625 | 54.55                        | 3 + 3.47 | 24288 | 46.32        |

| Table 5 – Engine exhaust composition at 4 bar IMEP and 1500 rpm. |
|---------------------------|---------------------------|---------------------------|
| CO₂ (%) | CO (ppm) | THC (ppm) | NO (ppm) | NO₂ (ppm) | N₂O (ppm) | NOx (ppm) | H₂O (%) | O₂ (%) |
| 5.3 | 127.5 | 577 | 750 | 40 | 0 | 790 | 5.1 | 15.1 |
Fig. 2 — NH₃ decomposition over Ru — Al₂O₃ catalyst: (a) 2 l/min (GHSV = 18000 h⁻¹) of pure ammonia decomposed at different temperatures, (b) 2–4 l/min of pure ammonia decomposition at different GHSV, and (c) ammonia conversion at different NH₃ concentrations in the NH₃—N₂ mixtures and temperatures.

Fig. 3 — Temperature profiles: (a) and (b) temperature profiles of NH₃ - ATR over 8 g and 16 g catalyst beds (c) temperature profiles of NH₃ exhaust gas reforming over 16 g catalyst bed.
amounts (in percentage) of NH₃ decomposed and oxidised are shown separately. The overall NH₃ conversion is presented as the sum of oxidised and decomposed NH₃ excluding any NH₃ slippage. As being consistent to the reaction’s thermal behaviour indicated in Fig. 3(a) and (b), the increased O₂/NH₃ ratio enhanced simultaneously the NH₃ oxidation and decomposition. Nevertheless, increasing O₂/NH₃ ratio to 0.175 did not further promote the NH₃ decomposition. However, it suppressed the NH₃ slippage through oxidation: the amount of NH₃ consumed in oxidation reached the maximum. It is also worth noticing that the O₂ content in each individual run was used completely, and no NO, NO₂ or N₂O formation was detected.

In addition to the NH₃ conversion, Fig. 4(b) – (d) plot the produced H₂ as a function of O₂/NH₃ ratio and the NH₃ inlet concentration (at each O₂/NH₃ ratio, see Table 4) for both of the NH₃ – ATR and NH₃ exhaust gas reforming. With more NH₃ decomposed at higher O₂/NH₃ ratios, higher H₂ production was achieved.

Furthermore, the NH₃ inlet concentration at every O₂/NH₃ ratio is identical for NH₃ – ATR over the 8 g and 16 g catalyst beds (the same projected area in Fig. 4 (b) and (c)). Therefore, the improved H₂ production at the 16 g bed confirmed the more favourable reaction conditions provided by the longer catalyst, and is in agreement with the temperature profiles discussed earlier.

Compared to the NH₃ – ATR at the 16 g catalyst, the NH₃ exhaust gas reforming over the same catalyst (Fig. 4(d)) was performed at lower inlet NH₃ concentration at each tested O₂/NH₃ ratio (due to the increased overall inlet flow, Table 4). Although the reactor temperature was reduced during the NH₃ exhaust gas reforming (Fig. 3(c)), at the same O₂/NH₃ ratio, hydrogen production is found to be approximately equivalent to that of the NH₃ – ATR. This observation can be explained by the NH₃ concentration effect shown in Fig. 2(c): less concentrated NH₃ in the exhaust allows ammonia decomposition to perform similarly to that of the NH₃ – ATR, but at lower temperatures.

The hydrogen efficiency (Eq. (4)) and reforming process efficiency (Eq. (5)) of the NH₃ exhaust gas reforming are shown in Fig. 5. Although the hydrogen efficiency was improved at high O₂/NH₃ ratios i.e. higher H₂ production, the reforming process efficiency decreased due to larger NH₃ consumption in exothermic oxidation. Thus a trade–off is shown between these efficiencies. It is suggested that applying the carbon–free reformate (as fuel) to an engine under a low O₂/NH₃ ratio (e.g. 0.06) is expected to be more beneficial in terms of diesel fuel replacement and the engine CO₂ emission.

3.3. Application of NH₃ exhaust gas reforming in diesel combustion and emission

In order to study how reformate produced under different efficiencies could affect engine combustion and emissions, the reformate was added into the engine’s intake and

Fig. 4 – (a) NH₃ conversion in NH₃ – ATR at different O₂/NH₃ ratios over 8 g and 16 g catalysts; dotted line: 16 g catalyst, solid line: 8 g catalyst. (b) – (d): H₂ production as a function of NH₃ concentration and O₂/NH₃ ratio; (b) NH₃ – ATR over 8 g catalyst, (c) NH₃ – ATR over 16 g catalyst and (d) NH₃ exhaust gas reforming over 16 g catalyst.
Reformate flow rates under different reactor conditions and their compositions in the engine intake.

Table 6 – Reformate flow rates under different reactor conditions and their compositions in the engine intake.

<table>
<thead>
<tr>
<th>O2/NH3</th>
<th>ηref (%)</th>
<th>ηH2 (%)</th>
<th>H2 (engine intake)</th>
<th>NH3 (engine intake)</th>
<th>Total reformate flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.06</td>
<td>102</td>
<td>67</td>
<td>2.6 l/min (5200 ppm)</td>
<td>1.05 l/min (2100 ppm)</td>
<td>3.65 l/min</td>
</tr>
<tr>
<td>0.12</td>
<td>95</td>
<td>78</td>
<td>2.9 l/min (5800 ppm)</td>
<td>0.47 l/min (940 ppm)</td>
<td>3.37 l/min</td>
</tr>
<tr>
<td>0.15</td>
<td>91</td>
<td>80</td>
<td>3.2 l/min (6340 ppm)</td>
<td>0.29 l/min (580 ppm)</td>
<td>3.49 l/min</td>
</tr>
<tr>
<td>0.175</td>
<td>88</td>
<td>77</td>
<td>3.0 l/min (6000 ppm)</td>
<td>0.28 l/min (580 ppm)</td>
<td>3.28 l/min</td>
</tr>
</tbody>
</table>

The addition of the reformate causes a reduction in brake thermal efficiency, but as the H2 concentration is increased the efficiency reduction decreases. However, Fig. 7(b) shows the use of reformate did result in a 4–5% reduction in injected diesel fuel (to maintain the engine speed and load). These observations indicate the reformate H2 worked as the primary substituent to the diesel fuel, while the NH3 was not combusted efficiently, as a result of its high auto – ignition resistance i.e. 651 °C. As shown by Fig. 7(c), with increased reformer – out NH3 slipping into the intake, the ammonia conversion during the combustion becomes less sufficient, which contributed primarily to the decreased brake thermal efficiency.

As for the engine emissions, replacing the primary diesel by non – carbon based reformate was able to reduce the engine – out carbon emissions. These are reflected by the decreased CO2, CO and THC shown in Fig. 7(d) – (f). However, with increased NH3 involved in the combustion, the NH3 concentration in the exhaust significantly increased, which was ranged from 90 ppm to almost 700 ppm. Apart from its poor combustion, the ammonia emission can also be related to NH3 being trapped in the combustion chamber crevices and when flame quenching on the chamber walls, i.e. the same mechanisms that are responsible for unburned hydrocarbons in Internal Combustion (IC) engines [16].

Fig. 8 shows the reformate addition increases the NOx emission, which is found in relation to the increased NH3 at the engine intake. As NH3 is nitrogen bounded, its oxidation in the combustion process allowed the formation of nitrogen oxides. Therefore, it reveals that the reformer out NH3 level needs to be controlled to maintain the NOx emission.

As well as the heightened overall NOx emission, the NO2/NO ratio is substantially increased compared to the pure diesel operation. Based on literature [38,39], this is thought to be caused by the well – known H2 effect. At low temperatures, peroxy radicals (HO2 and RO2) formed during combustion are crucial in promoting NO conversion into NO2. At relatively cooler in-cylinder temperatures associated with low/medium engine load conditions, a small portion of H2 – remains uncombusted [40], which can be then mixed with NO – rich combustion products and converted into NO2, which then reinforces the conversion of NO to NO2 [38]:

\[
\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH} \quad (7)
\]

\[
\text{RO}_2 + \text{NO} = \text{RO} + \text{NO}_2 \quad (8)
\]

The increased NO2 fraction in the engine exhaust is potentially beneficial as it can be utilised in catalytic aftertreatment systems for NOx and PM removal [41].

Conversely to the energetic benefits postulated earlier with the use of low oxygen to ammonia ratio in the reformer (Fig. 5), the observed engine combustion and emission suggest a use of high purity reformate hydrogen (reformer operated at high O2/NH3 ratio), as it is able to replace effectively the carbon fuels, minimise the emitted NH3 without affecting the engine performance. Although this will incur a reduction in the reforming process efficiency through higher NH3 oxidation, the amount of NH3 oxidised at the optimised O2/NH3 condition (0.15 in the current study, representing the reforming process that consumed the highest quantity of NH3 in the oxidative
portion) is calculated, using Eq. (9), to present only 1.3% of the total diesel fuel input at the studied engine condition, which indicates a reasonably small fuel penalty.

\[
\text{Fuel penalty} = \frac{\dot{m}_{\text{NH}_3} (\text{oxidised}) \times \text{LHV}_{\text{NH}_3}}{\dot{m}_{\text{ULSD}} (\text{input}) \times \text{LHV}_{\text{ULSD}}} \times 100% \tag{9}
\]

Where \( \dot{m} \) and LCV are the flow rate and calorific value of ULSD and ammonia respectively.

However, to continue using the studied catalyst it is necessary to improve the reactor geometry to reduce the heat loss and strengthen the average reactor temperature. The loss of heat generated both during and following the reaction can be used to improve the overall process efficiency. Recently, Kim et al. [42] provided a detailed study of a microreforming system, where a Micro – Combustor (for \( \text{NH}_3 \) combustion) and a Micro – Reactor (for \( \text{NH}_3 \) decomposition) are integrated in cylindrical/annular design for \( \text{H}_2 \) production. The system’s configuration is shown to be effective in heat – recirculation:

Fig. 6 – Engine in-cylinder pressure and rate of heat release at different reformate additions.

Fig. 7 – (a) engine brake thermal efficiency, (b) diesel fuel replacement, (c) \( \text{NH}_3 \) conversion during combustion, (d) \( \text{CO}_2 \) emissions, (e) total hydrocarbon emission, (f) \( \text{CO} \) emissions.
extracting heat from exhaust (reacted) gas for preheating fresh reactive mixtures. Hence a similar design can be adopted in the current reformer for better thermal management, leading to improved heat insulation and energy recovery. This would potentially increase the overall process efficiency and further suppress the fuel penalty.

4. Conclusions

From the study presented here, catalytic NH3 – ATR and ammonia exhaust gas reforming were investigated and proved feasible to produce H2 on board. The O2/NH3 ratio and its corresponding NH3 concentration in the gas feed as well as the GHSV were found to impact the H2 yield. A combination of these factors leads to different NH3 conversion, gas product composition and reaction efficiencies.

When the carbon – free reformate was introduced into the engine intake, part of the primary diesel was replaced and the engine’s carbon emissions (CO2, CO and THC) were reduced. The engine out NO2/NO ratio increased substantially, which is potentially beneficial to diesel aftertreatment system (DPF passive regeneration, SCR DeNOx activity at low temperature and etc.). However, excessive NH3 addition resulted in inefficient use of the reforming products, deteriorated engine out NOx emission level and undesired NH3 slippage in the exhaust. Hence, without engine modification/optimisation, the direct use of NH3 (as fuel) in diesel combustion could be regarded as inappropriate. Ammonia’s potential in delivering hydrogen should be magnified by adopting the studied reformer system, at conditions that produce high purity of H2. Nevertheless, the presence of NH3 in the exhaust could be beneficial to certain aftertreatment devices (NH3 – SCR), which will utilise the emitted NH3 in further reactions to control the overall engine emission.

Acknowledgements

The authors would like to thank Johnson Matthey for funding the project and providing the catalysts. The School of Mechanical Engineering at the University of Birmingham (UK) is gratefully acknowledged for the PhD School Scholarship to Mr. Wentao Wang. Engineering and Physical Science Research Council – EPSRC projects (EP/G038139/1) and the Advantage West Midlands and the European Regional Development Fund as part of the Science City Research Alliance Energy Efficiency Project are also acknowledged for supporting the research work.

R E F E R E N C E S


