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Exhaust Energy Recovery via Catalytic Ammonia Conversion to Hydrogen for Low Carbon Clean Vehicles

S. Sittichompoo¹, H. Nozari¹, J.M. Herreros¹, N. Serhan¹, J. A.M. da Silva², A.P.E. York³
P. Millington³, A. Tsolakis¹*

¹School of Mechanical Engineering, University of Birmingham, Edgbaston, UK
²Department of Mechanical Engineering, Federal University of Bahia, Salvador, Brazil
³Johnson Matthey, Blounts Court, Sonning Common, Reading, RG4 9NH, UK

*Corresponding author: a.tsolakis@bham.ac.uk

Abstract

The work presented here, demonstrates the on-board exhaust assisted catalytic ammonia (NH₃) conversion to H₂-N₂ using either only exhaust heat (decomposition) or by direct reaction with part of the exhaust gas (reforming). The resultant H₂-N₂ gas mixture from the exhaust heat driven thermochemical energy recovery processes contains up to 15% more energy than the reactant NH₃ (i.e. for 1kW of NH₃ used in the reaction up to 1.15kW of H₂ is produced).

Experimental studies using a rhodium-platinum (Rh-Pt) catalyst and equilibrium calculations in Chemkin using Konnov’s 0.6 and Nozari’s reduced mechanisms have revealed that complete NH₃ conversion occurs at typical gasoline direct injection (GDI) engine exhaust gas temperatures (450°C – 550°C).

By partially replacing gasoline in GDI engine with the resultant (H₂-N₂ products, up to 30% reduction in CO₂ and fuels consumption can be achieved. Additional benefits can be gained under real engine operation when the benefits of reduced pumping losses, due to intake dilution with H₂-N₂ gas, are also considered. Furthermore, the work demonstrates additional benefits in CO₂ life cycle for the NH₃ use as an energy carrier in transportation and broader combustion power generation systems.
Keywords: ammonia decomposition; reforming catalyst; hydrogen production; energy recovery; gasoline engine emission.

Highlights:
- GDI engine exhaust energy is recovered for on-board NH₃ decomposition.
- Exhaust assisted NH₃ decomposition was achieved between 450°C – 650°C.
- NH₃ reforming was performed by recovering heat and mixing directly with a part of exhaust gases.
- Up to 30% improvement in GDI fuel economy and CO₂ reduction can be achieved.
- NH₃ production by renewable methods have potential of further reducing CO₂ emission.

Introduction

Hydrogen (H₂) has shown benefits as an energy vector in transportation, either in combustion or fuel cell applications and can also be used, in significantly lower quantities, to improve the combustion process of liquid and gaseous fuels and enhance the performance of the catalytic technologies in reducing emissions [1]–[3]. However, due to hydrogen’s low volumetric energy density in comparison to widely used fuels [4], storage at high pressures is required which in turn necessitates additional energy use for its compression.

Ammonia carries more hydrogen atom per one mole than one mole of hydrogen (H₂), and has higher energy density per volume than that of hydrogen. Furthermore, ammonia can be stored as liquid at atmospheric pressure and relatively reasonable temperatures (lower than -34 °C) which results in much cheaper and simpler storage tanks in comparison to hydrogen cylinders. In terms of safety, ammonia has higher ignition temperature than hydrogen. In addition, cost per mass and per unit energy of ammonia is less than that of hydrogen [5] due to widely implemented ammonia production infrastructures [6]. Approximately 180 million tons (Mt.) of NH₃ are produced annually (globally) with about 12% (21 Mt.) produced in Europe [7]. The expected yearly growth of NH₃ production of 1.0 to 1.5%
ensures the availability of NH$_3$ for wide scale usage. Also, the use of renewable energy for ammonia production has high potential to reduce overall CO$_2$ emission within NH$_3$ life cycle, making ammonia usage even more reasonable and attractive.

There are some studies available in the literature using ammonia in internal combustion engines as a stand-alone fuel [9] and in dual-fuel mode with conventional liquid fuels (diesel [10], gasoline [6]) or with alternative fuels such as DME [11]. NH$_3$ has been also utilised in combination with H$_2$, for example; as synthetic NH$_3$ and H$_2$ [12] or using Ru-catalyst based NH$_3$ cracking reactor to generate H$_2$ (with trace of NH$_3$) and co-injected with NH$_3$ [13], [14]. Noted that exhaust gas was not utilized as reactant for decomposition process. NH$_3$-H$_2$ fuelled engine performances [15] and nitrogen-base emissions from NH$_3$-H$_2$ fueled engine [16] have been investigated for both compression and spark ignition engines. In general, fuelling with NH$_3$ showed significant CO$_2$ reduction and increased CO, HCs, NH$_3$ and NO$_x$ emissions. Due mainly to ammonia properties and combustion characteristics such as low flame velocity, low flame temperature and high ignition energy, results for example in poor engine performance with respect to gasoline combustion [12], with potential of ammonia slippage. These considerations make the direct use of ammonia in the engine technology less practical. Studies showed that small amount of H$_2$ could be used to promote NH$_3$ combustion. [12]–[16] On-board hydrogen production through the decomposition of ammonia either by only utilising the heat (eq.1) or by utilising heat and exhaust species such as O$_2$ are shown in eq.1 and eq.2, respectively. Stored ammonia has advantages over storing hydrogen in highly pressurized vessels when applied to passenger vehicles [12] and is in accordance to Department of Energy (DOE).

\[
\text{NH}_3 \text{ Decomposition:} \quad 2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2 \quad \Delta H^\circ = 46.19 \text{ kJ/mol} \tag{1}
\]

\[
\text{NH}_3 \text{ Decomposition with exhaust:} \quad \text{NH}_3 + x\text{O}_2 \rightarrow 2x\text{H}_2\text{O} + (1.5 - 2x) \text{H}_2 + 0.5\text{N}_2; \text{ if } x < 0.75; \tag{2}
\]

In earlier work, we have demonstrated the thermochemical heat recovery technique named “exhaust gas fuel reforming” where part of the engine exhaust, reacts with fuel to
produce hydrogen rich gas with higher energy content than the fuel used in the reaction. [17]

By replacement of part of the gasoline fuel in the GDI engine combustion process with the higher energy content H₂-rich gas produced by reforming, simultaneously improvements in engine fuel economy and oxides of nitrogen (NOx) and particulate matter (PM) emissions were seen.

In the case of ammonia, in addition of using only the exhaust heat for its decomposition (eq.1), ammonia can also serve as a direct reactant with the exhaust constituents to promote reactions such as oxidative reforming, and provide a COx-free reforming process (eq.2); this helps in the decarbonisation of road transport. The H₂-rich gas with trace of unconverted NH₃ will be reintroduced in the combustion chamber via intake manifold where NH₃ will be combusted with assistance of H₂ to minimise NH₃ slippage. This can also address the potential low temperature activity, since the CO, THC and expected small portion of ammonia can be oxidised within the reactor to provide sufficient temperature for the subsequent endothermic reactions (eq.2) [5].

Ruthenium (Ru) catalyst has been considered the most active catalyst for NH₃ decomposition and also for NH₃ oxidation [4], [18], however, its scarcity seems to limit the usage in large scale [19]–[21]. Rhodium-platinum (Rh-Pt) catalyst is a contender candidate for exhaust gas reforming due to its successful in reforming HCs fuels [17], [22], [23] and selectivity toward NH₃ decomposition of rhodium and NH₃ oxidition of platinum. Hence, Rh-Pt based catalyst can potentially be utilised as sharing catalyst for reforming both HCs fuels and NH₃.

The aim of this study is to investigate ammonia decomposition either by only utilising the heat of a modern GDI engine exhaust (eq.1) or by reaction with part of the exhaust (eq.2) for on-board H₂ production using rhodium-platinum catalyst. In both cases the exhaust gas heat drives the endothermic reactions, but in eq.2, additional species from the exhaust may participate in the reactions. The study then assesses the conditions required for almost complete ammonia decomposition to H₂-N₂ with increased energy content by up to 15% when
compared to feed ammonia. A theoretical study then provides an estimation of the potential fuel and CO\textsubscript{2} saving when the H\textsubscript{2}-N\textsubscript{2} is used for combustion in GDI vehicles.

**Experimental**

**Instruments and setups**

The NH\textsubscript{3} decomposition experiments are conducted on a specific designed setup shown in figure 1. The data acquisition is performed to capture volumetric output flow of gaseous species such as NH\textsubscript{3}, N\textsubscript{2}O, NO\textsubscript{x}, CO, CO\textsubscript{2}, and THC using a MKS Multigas 2030 FTIR with data sampling resolution of 1.0 second. Oxygen concentration is measured by a Pierburg Instrument HGA400. Meanwhile, the amount of H\textsubscript{2} output is measured by a H-Sense mass spectrometer from V&F Analyse- und Messtechnik GmbH.

A Rh-Pt hydrocarbon catalyst with dimensions of 22 mm diameter and 77 mm length (0.0293 litre of projected volume) is mounted in a stainless-steel tube reactor installed in a temperature-controlled furnace. K-type thermocouples are installed to monitor inlet and outlet gas temperatures which are connected to TC08 Picolog for data logging with time sampling resolution of 1.0 second.

![Experimental schematic diagram](image)

**Figure 1** Experimental schematic diagram.
Methodology

A known rhodium-platinum (Rh-Pt) catalyst previously developed for fuel reforming studies is now utilised in the NH₃ decomposition experiments. The catalyst temperature was controlled with an electric furnace to mimic the engine exhaust gas conditions. Reactor temperature is a crucial parameter in the experiments and is controlled in the range between 450°C and 650°C which resembles real exhaust gas temperatures from the gasoline engine in medium to high engine loads. In this study, the NH₃ was diluted in nitrogen (5% NH₃-vol in N₂). Gas Hourly Space velocity (GHSV), decomposition/reforming process efficiency and ammonia conversion efficiency are calculated using eq.3 to eq.5.

The decomposition/reforming process efficiency in eq.4 is calculated based on the ratio of amount of energy of product (H₂ + NH₃,unconverted) to reactant (NH₃) which can be greater than 100% due to heat recovery by endothermic reaction leading to the significant high lower heating value (LHV) of hydrogen. For instance, if the maximum theoretical hydrogen is produced from 1 mole of ammonia, then it would yield the maximum hydrogen production efficiency of 115% (approx.) (eq.1).

\[
GHSV(h^{-1}) = \frac{\text{Gas flow rate (lpm)} \times 60}{\text{catalyst volume (l)}} \tag{3}
\]

\[
\eta_{ref} = \frac{\left( LHV_{H_2} \times \dot{m}_{H_2} \right) + \left( LHV_{NH_3} \times \dot{m}_{NH_3} \right)}{LHV_{NH_3} \times \dot{m}_{NH_3}} \times 100\% \tag{4}
\]

\[
NH_3_{conversion} = \left( \frac{NH_3_{inlet} - NH_3_{outlet}}{NH_3_{inlet}} \right) \times 100\% \tag{5}
\]

Eq.4 only takes as an energy input the supplied NH₃ and disregards energy from other gases H₂, CO and THC part of the GDI engine’s exhaust gas. This intrinsic energy in the exhaust gas is considered as ‘free’ energy in this context.
A 2L turbo-charged gasoline direct injection (GDI) engine on an engine dynamometer is utilised to produce exhaust gas for NH$_3$ reforming. The engine load of 35 Nm at 2100 rpm is chosen corresponding to New European Drive Cycle (NEDC) for mid-size to large family vehicle with 2L displacement engine. Exhaust gas composition shown in Table 1 was analysed with the use of an MKS FTIR gas analyser.

**Table 1** Exhaust gas compositions from GDI engine.

<table>
<thead>
<tr>
<th>Exhaust source</th>
<th>CO (ppm)</th>
<th>CO$_2$ (%)</th>
<th>THC (ppm)</th>
<th>NO (ppm)</th>
<th>NO$_2$ (ppm)</th>
<th>H$_2$O (%)</th>
<th>O$_2$ (%)</th>
<th>H$_2$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bTWC</td>
<td>6756</td>
<td>11.4</td>
<td>1521</td>
<td>565</td>
<td>1.5</td>
<td>13.2</td>
<td>0.7</td>
<td>2289</td>
</tr>
</tbody>
</table>

Equilibrium calculation of NH$_3$ decomposition is performed using Chemkin software applying Konnov-0.6 mechanism [24] and Nozari’s reduced mechanism [25], [26]. The new updates introduced by Konnov et al. [27] are also implemented in the mechanism. Konnov reaction mechanism is one of the renowned and widely used mechanisms in H-N-O chemistry with its accuracy been validated by several experimental and numerical studies in the literature [28], [29]. Meanwhile, equilibrium calculation of NH$_3$ reforming in gasoline exhaust gas is implemented. A constant pressure and enthalpy setting are applied with temperature ranging between 450 to 650°C and at the pressure of 1 atm.

**NH$_3$ decomposition**

Experiments are performed to observe the H$_2$ production efficiency and NH$_3$ conversion in the presence of the Rh-Pt catalyst. Inlet NH$_3$ concentration of 1.00%, 2.00% and 4.45% by volume in N$_2$ are selected to study the NH$_3$ decomposition rates and H$_2$ production. In real life application N$_2$ dilution is not required and hence the full flow can consist of ammonia. Assuming that the reaction rates of the ammonia decomposition won’t be affected significantly and based on the volume of the catalyst used in this study, the output power of the reformate in the full-scale catalyst will be estimated. GHSV values between 16,000 and 20,000 h$^{-1}$ are selected based on previous studies [5], [30]. All tests are performed at temperature of 450,
550 and 650°C, to mimic typical GDI engine exhaust temperature. The ammonia lower heating value of 18.646 MJ/kg was selected for the calculations of power input and the process efficiency. Test conditions are illustrated in table 2.

Table 2 Test conditions for NH₃ decomposition in N₂.

<table>
<thead>
<tr>
<th># Test</th>
<th>Total GHSV (h⁻¹)</th>
<th>NH₃ (%vol.)</th>
<th>NH₃ flow rate (g/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16000</td>
<td>1.00</td>
<td>3.4</td>
</tr>
<tr>
<td>2</td>
<td>16000</td>
<td>2.00</td>
<td>6.7</td>
</tr>
<tr>
<td>3</td>
<td>16000</td>
<td>4.45</td>
<td>14.9</td>
</tr>
<tr>
<td>4</td>
<td>20000</td>
<td>4.45</td>
<td>18.7</td>
</tr>
</tbody>
</table>

NH₃ reforming in real GDI engine exhaust gas

For this test NH₃ concentration of 1%-vol (corresponding to 3.358 g/hₙ₃ or 17.4W power input into the reactor) in the mixture is selected for the reactions with exhaust gas that was obtained before Three-Way Catalyst (bTWC) of the GDI engine. Exhaust gas bTWC contains ~0.7%O₂ and other gas compositions as can be seen in Table 1. The volumetric exhaust gas flow rates (defined as ‘%Exhaust-vol’) are adjusted to provide O₂/NH₃ ratio between 0.078 to 0.313 as shown in Table 3. In this case, and in contrast to the study above, the available CO, HC and H₂ (Table 1) in the engine exhaust will be utilised in the oxidation reactions to provide additional heat and increase the catalyst temperature. As the engine test is carried out at 35 Nm engine torque and 2100 rpm engine rotational speed, the catalyst inlet temperature of 650°C is chosen to match the actual exhaust temperature.
Table 3 Test conditions for NH₃ reforming using engine exhaust gas

<table>
<thead>
<tr>
<th>#</th>
<th>Condition</th>
<th>O₂/NH₃</th>
<th>H₂O/NH₃</th>
<th>%NH₃-vol</th>
<th>%Exhaust-vol</th>
<th>%N₂-vol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>0.078</td>
<td>1.645</td>
<td>1.0</td>
<td>12.5</td>
<td>86.5</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>0.234</td>
<td>3.705</td>
<td>1.0</td>
<td>28.2</td>
<td>70.8</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>0.313</td>
<td>5.015</td>
<td>1.0</td>
<td>38.1</td>
<td>60.9</td>
</tr>
</tbody>
</table>

Results and Discussion

NH₃ decomposition and exhaust energy recovery studies

Equilibrium calculations predict complete NH₃ decomposition at the lowest GDI engine exhaust temperature range of 400°C, while the experimental results using the Rh-Pt catalyst show that almost complete decomposition of NH₃ was achieved at 550°C. The results demonstrate a strong dependence to temperature and to NH₃ concentration up to a limit [4], emphasizing the kinetically limited reactions for a set temperature. As shown in Fig. 2 (Left), for inlet NH₃ of 3.4 g/h (corresponding to 1%-vol concentration) in the micro-reactor at 550°C or higher, almost complete conversion to H₂ was achieved. At 550°C the process efficiency for 14.5 g/h (4.45%-vol concentration) NH₃ case is 111.2%, meaning that when 76W of NH₃ enters the mini reactor, due to energy (exhaust heat) recovery of about 9W, 85W of H₂-rich mixture was produced.

Figure 2 Decomposition process efficiency (Left) and NH₃ conversion efficiency (%) (Right).
Higher H₂ production (mass), reformer power output and thus exhaust energy recovery, can be achieved by increasing NH₃ concentration (Fig. 2). However, this could impact on NH₃ decomposition rates depending on the range utilised (Fig. 2). This is a trend that is also dependent on the exhaust gas temperature and available amount of exhaust gas.

For a full-scale engine application where up to a half a litre size NH₃ decomposition catalyst can be used the potential energy recovery, taking into account results from conditions 3 and 4 in table 2, will be in the range of 2.77 kW to 3.99 kW (Fig. 3) when 23.76 kW and 29.69 kW of NH₃ input is used, respectively.

The potential of CO₂ reduction by utilising H₂ produced from NH₃ by exhaust heat energy recovery can be estimated based on the decomposition process efficiency from our experiments. Based on an engine condition of 148 Nm, 2500rpm, which represents typical engine torque and speed for multi-cylinder gasoline engine [23], the system has potential to simultaneously reduce fuel consumption and CO₂ emission up to 30%. Additional benefits can be gained under real engine operation as suggested by Fennell et al. [22], as the introduction of decomposed NH₃ to the engine through the EGR loop can reduce pumping losses under some conditions and further improve engine efficiency and reduce CO₂ emissions.

Figure 3 Potential energy recovery (Left) and gasoline & CO₂ reduction (Right) by direct NH₃ decomposition calculated from GDI engine conditions at 148 Nm/2500 rpm at different NH₃ inputs.
Although increasing the GHSV by 25% from 16,000 h\(^{-1}\) to 20,000 h\(^{-1}\), and hence the NH\(_3\) flow rate (laboratory scale) from 14.9 g/h to 18.7 g/h, demonstrates an additional decrease in both NH\(_3\) decomposition rates and process efficiency (Fig. 4) at temperatures below 550°C, the exhaust heat recovery was improved. The decreased NH\(_3\) decomposition efficiency was due mainly to the reduced residence time (or contact time [31]) between gas and catalyst surface. Additionally, the NH\(_3\) decomposition process is limited by the rate of NH\(_3\) adsorption onto the catalyst active site; this is followed by N-H bond cleavage, N recombination, and desorption of dinitrogen [4], [32] at temperatures below 377°C (650K) [33]. Nitrogen desorption is considered as the rate-limiting step of NH\(_3\) decomposition [34]. The decomposition process efficiency is marginally decreased at higher temperature (650°C) and significantly at lower catalyst temperatures (i.e. at 550°C) due mainly to heat transfer deficiency, that restricts the decomposition process to reach its ideal equilibrium [31].

![Figure 4 Effect of GHSV on decomposition process efficiency and NH\(_3\) conversion efficiency.](image)

**Figure 4** Effect of GHSV on decomposition process efficiency and NH\(_3\) conversion efficiency.

Figure 5 (Left) illustrates the heat requirement to decompose ammonia based on ammonia’s theoretical enthalpy of reaction (\(\Delta H^0\)) and available exhaust heat from engine at 148 Nm/2500 rpm assuming an exhaust gas exergy coefficient from GDI engine in Fennell et
al. [17]. At an NH₃ input rate of 29.7 kW, 4.3 kW of heat is required for complete decomposition, which is well under the heat availability limit in the exhaust gas. Estimations of available exhaust heat at typical engine operating conditions for a multi-cylinder gasoline engine [23] are illustrated in figure 5 (Right).

**Figure 5** Exhaust heat exergy availability for NH₃ decomposition (Left) and available exhaust heat at different engine conditions.

The ICCT (International Council on Clean Transportation) [35] reported that average current passenger vehicles in the European market comply to the 2015 CO₂ emission limit regulations. However, current commercial vehicles are still unable to fulfil the CO₂ emission regulation limit 2020/21 target with current emission control technologies. Fig. 6 shows the predicted value of potential CO₂ reduction by utilising H₂ produced from NH₃ by exhaust heat energy recovery, which demonstrates the possibility (with optimisation of catalyst choice, GHSV and heat transfer of reformer) to further decrease the amount of CO₂ emitted from internal combustion engines up to 30.4% based on the process efficiency from our experiments. This thermochemical energy recovery technique with optimisation has potential to enable passenger vehicles to meet 2020/21 and beyond CO₂ emission targets.
**Figure 6** Passenger vehicle predicted CO$_2$ reduction by thermochemical energy recovery technology using ammonia.

**NH$_3$ reforming in direct reaction with gasoline engine exhaust gas**

**Prediction and experimental results of reformate compositions**

Figure 7 shows the equilibrium calculations that predict the NH$_3$ reforming in reaction with the engine exhaust gas (O$_2$/NH$_3$ = 0.234) at different temperatures. The partitioning [36] equilibrium calculations are designed to confirm the effect of NH$_3$ presence on H$_2$ production. The calculations predict that H$_2$ produced by steam reforming (SR) and water gas shift (WGS) from hydrocarbon components in GDI exhaust forms approximately 20% of the H$_2$ available in the reformate. The remaining H$_2$ in the reformate is assumed to result from NH$_3$ decomposition. Meanwhile, all available O$_2$ in inlet mixtures will be consumed mainly by oxidation, while trace amounts of NH$_3$ and THC can be found in the product reformate. H$_2$ yield is increased with catalyst temperature as NH$_3$ reforming and steam reforming are enhanced. At higher temperature, the methanation reaction is suppressed and the reverse WGS reaction is more favoured, which leads to the slight decline of H$_2$ produced [37].
Figure 7 Equilibrium prediction of NH₃ reforming with GDI engine exhaust gas at O₂/NH₃ = 0.234.

Figure 8 shows predicted and experimental reformate gas compositions from NH₃ reforming with GDI engine exhaust at catalyst inlet temperature of 650°C at different O₂/NH₃ ratios. For experimental results, at low O₂/NH₃ ratio (0.078), reforming using bTWC exhaust gas produces a large amount of H₂ due to less input O₂, which limits H₂ and NH₃ consumption by H₂ + 0.5O₂, NH₃ + O₂ and 4NO + 4NH₃ + O₂ reactions. [36], [38] As O₂/NH₃ increased (more exhaust in the mixture), output H₂ concentration is reduced and more unconverted NH₃ is observed, mainly because the H₂ + 0.5O₂ reaction is more pronounced and catalytic NH₃ decomposition is inhibited by H₂O presence [39]. Increasing O₂/NH₃ worsens catalytic performance by introducing more H₂O and, as a result, as much as 48.66% of unconverted NH₃ can be observed. This means 5134 ppm-NH₃ is converted into 7701 ppm-H₂ at theoretical conversion efficiency. Hence, approximately 1500 ppm-H₂ is assumed to be derived from other reaction pathways.

Additional reaction pathways for formation of NH₃ are NO + 2.5H₂ → NH₃ + H₂O and NO + CO + 1.5H₂ → NH₃ + CO₂, both of which consume H₂ resulting in decreased H₂ yield and increased NH₃ output. The in-situ NH₃ formation is driven by the high selectivity of Pt catalyst toward NH₃ formation, as reported in literature [36].
**Figure 8** Prediction and experimental reformate compositions from NH$_3$ reforming with GDI exhaust gas.

**Reforming process efficiency and NH$_3$ conversion**

Figure 9 shows the predicted and experimental reforming process efficiencies and NH$_3$ conversion efficiencies for NH$_3$ reforming using GDI engine exhaust gases. Overall, reforming process efficiency obtained from experimental results indicate similar trends to the equilibrium calculation, although the experiments show lower NH$_3$ conversion efficiency. However, the
significant amount of NH\textsubscript{3} slippage in the experiments contributes to the energy content of the reformate, comparable reforming process efficiencies are obtained.

The scale-up prediction for full scale application is based on the same NH\textsubscript{3} input energy density (table 2) as discussed in NH\textsubscript{3} direct decomposition results. The recovered fuel energy (Fig. 10 Left) increased as function of O\textsubscript{2}/NH\textsubscript{3} ratio in the same trend as reforming process efficiency as shown in Fig. 9 (Left). The NH\textsubscript{3}-exhaust reforming at O\textsubscript{2}/NH\textsubscript{3} ratio above 0.078 reveals the potential to recover more energy than direct NH\textsubscript{3} decomposition due mainly to the assistance of the autothermal-reforming process (ATR) [5], [22], [23] which generates additional heat to sustain the endothermic reforming reactions. However, at low O\textsubscript{2}/NH\textsubscript{3} ratio (0.078), the results indicate a negative value of fuel energy recovery (Fig. 10 left) which means some input fuel energy is lost in the process mainly by oxidation or partial oxidation of H\textsubscript{2}.

On the other hand, the predicted value of gasoline saved and CO\textsubscript{2} reduced by utilising reformate in the REGR (Reformed-exhaust gas recirculation) configuration [30] in the GDI engine at 148 Nm and 2500 rpm are illustrated in Fig. 10 (Right). In this prediction, only energy from H\textsubscript{2} and NH\textsubscript{3} are taken into account and it is assumed that all H\textsubscript{2} and NH\textsubscript{3} fed into the engine will be converted into energy by combustion. As H\textsubscript{2} and NH\textsubscript{3} are CO\textsubscript{x}-free species the amount of %fuel saved and %CO\textsubscript{2} reduced are identical. In this case, marginal improvement
of gasoline and CO₂ reduction could be seen in comparison to the direct NH₃ decomposition experiment (30.43% by NH₃ direct decomposition versus 31.96% by NH₃ exhaust reforming).

In a real operating scenario, other gas components (e.g. CO and HCs) in the reformate will also be fed into the engine intake manifold. Therefore, the % gasoline saved can be marginally enhanced if assuming CO and HCs are combustible. However, there will be a trade-off with the %CO₂ reduction as some carbon components will also be introduced along with the reformate.

**Figure 10** Potential energy recovery (Left) and gasoline & CO₂ reduction (Right) by NH₃-exhaust gas reforming calculated from GDI engine conditions at 148 Nm/2500 rpm at different O₂/NH₃ ratios.

### Ammonia and gasoline energy life cycle and carbon footprint

Figure 11 shows the CO₂ emission and energy consumption required for ammonia production in comparison to gasoline production under different routes (refer to table 4 for the plot legends). The most common route is the production of synthesis gas via steam methane reforming (SMR), points 1A, 4A, 5A and 7A. For this production route, CO₂ emissions range from 76 gCO₂/MJ to 112 gCO₂/MJ while energy consumption varies from 1.35 kJ/kJ to 2.00 kJ/kJ. Gasoline production and usage are responsible for emissions of about 80 gCO₂/MJ and consumes about 1.17 kJ/kJ for production. This means that the use of ammonia from the most efficient production processes applying the most used technology provides a decrease of
about 5% in CO$_2$ emissions in comparison with the use of gasoline. When the on-board fuel reforming efficiency increment (30%) is taken into consideration, the reduction in CO$_2$ emissions can reach up to 30% for each MJ of fuel replaced. Furthermore, ammonia production is moving away from using fossil feedstocks towards electrification using hydrogen made by electrolysis [40], points 8A to 11A. For these routes a potential reduction of up to 75% in CO$_2$ emissions can be expected.

**Table 4** Summary of exergy and CO$_2$ footprint of fuel productions.

<table>
<thead>
<tr>
<th>Fig.11 designation</th>
<th>Fuel</th>
<th>Energy cost (kJ/J)</th>
<th>CO$_2$ cost (gCO$_2$/MJ)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
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**Figure 11** Comparative amounts of CO$_2$ emissions and energy required for ammonia and gasoline productions.

**Conclusions**

The main scope of this study was to investigate energy recovery from vehicle exhaust via catalytic NH$_3$ conversion for on-board H$_2$ production. This is through applying a promising and practical method using NH$_3$ which enables partial replacement of the gasoline fuel with on-board produced CO$_x$-free H$_2$. The performance evaluation of the NH$_3$ conversion technique is done under two different circumstances: using only the exhaust heat for decomposing ammonia and using a part of the exhaust heat and components for thermochemical recovery via ammonia reforming.

In both investigated methods, the results show a significant potential in improving the fuel economy and reducing the CO$_2$ emissions of the engine. While ammonia reforming by
extracted exhaust heat resulted in a 30% improvement in fuel economy and, therefore CO₂ emissions. NH₃ reforming with exhaust gas leads to an improvement of up to 32%. CO₂ life cycle analysis of NH₃ production routes also reveals that alternative NH₃ production methods (e.g. using renewable energy in the process) offer a potential to further reduce CO₂ emissions per unit of NH₃ in comparison to gasoline. It is concluded that using ammonia for exhaust reforming can have a significant impact on reducing the carbon footprint of road vehicles. This is well aligned with the decarbonization of the road transport and meeting the net zero carbon aspiration of the countries around the globe.

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