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

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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 NH_3 decomposition.
- Exhaust assisted NH_3 decomposition was achieved between 450°C – 650°C
- NH_3 reforming was performed by recovering heat and mixing directly with a part of exhaust gases.
- Up to 30% improvement in GDI fuel economy and CO_2 reduction can be achieved.
- NH_3 production by renewable methods have potential of further reducing CO_2 emission.

Introduction

Hydrogen (H_2) 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 (H_2), 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 NH_3 are produced annually (globally) with about 12% (21 Mt.) produced in Europe [7]. The expected yearly growth of NH_3 production of 1.0 to 1.5%

[8] ensures the availability of NH₃ for wide scale usage. Also, the use of renewable energy for ammonia production has high potential to reduce overall CO₂ emission within NH₃ 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]. NH₃ has been also utilised in combination with H₂, for example; as synthetic NH₃ and H₂ [12] or using Ru-catalyst based NH₃ cracking reactor to generate H₂ (with trace of NH₃) and co-injected with NH₃ [13], [14]. Noted that exhaust gas was not utilized as reactant for decomposition process. NH₃-H₂ fuelled engine performances [15] and nitrogen-base emissions from NH₃-H₂ fueled engine [16] have been investigated for both compression and spark ignition engines. In general, fuelling with NH₃ showed significant CO₂ reduction and increased CO, HCs, NH₃ 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 H₂ could be used to promote NH₃ 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 O₂ 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).

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

79 produce hydrogen rich gas with higher energy content than the fuel used in the reaction. [17]
80 By replacement of part of the gasoline fuel in the GDI engine combustion process with the
81 higher energy content H₂-rich gas produced by reforming, simultaneously improvements in
82 engine fuel economy and oxides of nitrogen (NO_x) and particulate matter (PM) emissions were
83 seen.

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

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

100 The aim of this study is to investigate ammonia decomposition either by only utilising
101 the heat of a modern GDI engine exhaust (eq.1) or by reaction with part of the exhaust (eq.2)
102 for on-board H₂ production using rhodium-platinum catalyst. In both cases the exhaust gas
103 heat drives the endothermic reactions, but in eq.2, additional species from the exhaust may
104 participate in the reactions. The study then assesses the conditions required for almost
105 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 CO₂ saving when the H₂-N₂ is used for combustion in GDI vehicles.

Experimental

Instruments and setups

The NH₃ 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 NH₃, N₂O, NO_x, CO, CO₂, 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 H₂ 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.

Figure 1 Experimental schematic diagram.

Methodology

A known rhodium-platinum (Rh-Pt) catalyst previously developed for fuel reforming studies is now utilised in the NH_3 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 NH_3 was diluted in nitrogen (5% NH_3 -vol in N_2). 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 ($\text{H}_2 + \text{NH}_{3,\text{unconverted}}$) to reactant (NH_3) 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).

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

$$\eta_{ref} = \frac{\left((LHV_{H_2} \times \dot{m}_{H_2}) + (LHV_{NH_3} \times \dot{m}_{NH_3}) \right)_{\text{product}}}{(LHV_{NH_3} \times \dot{m}_{NH_3})_{\text{reactant}}} \times 100\% \quad (4)$$

$$NH_{3\text{ conversion}} = \left(\frac{NH_{3\text{ inlet}} - NH_{3\text{ outlet}}}{NH_{3\text{ inlet}}} \right) \times 100\% \quad (5)$$

Eq.4 only takes as an energy input the supplied NH_3 and disregards energy from other gases H_2 , 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.

Exhaust source	CO (ppm)	CO ₂ (%)	THC (ppm)	NO (ppm)	NO ₂ (ppm)	H ₂ O (%)	O ₂ (%)	H ₂ (ppm)
bTWC	6756	11.4	1521	565	1.5	13.2	0.7	2289

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.

NH₃ 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 reformat 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.

# Test	Total GHSV (h ⁻¹)	NH ₃ (%vol.)	NH ₃ flow rate (g/h)
1	16000	1.00	3.4
2	16000	2.00	6.7
3	16000	4.45	14.9
4	20000	4.45	18.7

NH₃ reforming in real GDI engine exhaust gas

For this test NH₃ concentration of 1%-vol (corresponding to 3.358 g/h_{NH₃} 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

# Condition	O ₂ /NH ₃	H ₂ O/NH ₃	%NH ₃ -vol	%Exhaust-vol	%N ₂ -vol
1	0.078	1.645	1.0	12.5	86.5
2	0.234	3.705	1.0	28.2	70.8
3	0.313	5.015	1.0	38.1	60.9

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 H_2 production (mass), reformer power output and thus exhaust energy recovery, can be achieved by increasing NH_3 concentration (Fig. 2). However, this could impact on NH_3 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 NH_3 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 NH_3 input is used, respectively.

The potential of CO_2 reduction by utilising H_2 produced from NH_3 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 CO_2 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 NH_3 to the engine through the EGR loop can reduce pumping losses under some conditions and further improve engine efficiency and reduce CO_2 emissions.

Figure 3 Potential energy recovery (Left) and gasoline & CO_2 reduction (Right) by direct NH_3 decomposition calculated from GDI engine conditions at 148 Nm/2500 rpm at different NH_3 inputs.

Although increasing the GHSV by 25% from 16,000 h⁻¹ to 20,000 h⁻¹, and hence the NH₃ flow rate (laboratory scale) from 14.9 g/h to 18.7 g/h, demonstrates an additional decrease in both NH₃ decomposition rates and process efficiency (Fig. 4) at temperatures below 550°C, the exhaust heat recovery was improved. The decreased NH₃ decomposition efficiency was due mainly to the reduced residence time (or contact time [31]) between gas and catalyst surface. Additionally, the NH₃ decomposition process is limited by the rate of NH₃ 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 NH₃ 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 NH₃ conversion efficiency.

Figure 5 (Left) illustrates the heat requirement to decompose ammonia based on ammonia's theoretical enthalpy of reaction (ΔH°) 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 NH_3 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 NH_3 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 CO_2 emission limit regulations. However, current commercial vehicles are still unable to fulfil the CO_2 emission regulation limit 2020/21 target with current emission control technologies. Fig. 6 shows the predicted value of potential CO_2 reduction by utilising H_2 produced from NH_3 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 CO_2 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 CO_2 emission targets.

Figure 6 Passenger vehicle predicted CO₂ reduction by thermochemical energy recovery technology using ammonia.

NH₃ reforming in direct reaction with gasoline engine exhaust gas

Prediction and experimental results of reformat compositions

Figure 7 shows the equilibrium calculations that predict the NH₃ 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 NH₃ presence on H₂ production. The calculations predict that H₂ produced by steam reforming (SR) and water gas shift (WGS) from hydrocarbon components in GDI exhaust forms approximately 20% of the H₂ available in the reformat. The remaining H₂ in the reformat is assumed to result from NH₃ decomposition. Meanwhile, all available O₂ in inlet mixtures will be consumed mainly by oxidation, while trace amounts of NH₃ and THC can be found in the product reformat. H₂ yield is increased with catalyst temperature as NH₃ 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 H₂ 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_3 slippage in the experiments contributes to the energy content of the reformat, comparable reforming process efficiencies are obtained.

Figure 9 Effect of different O_2/NH_3 ratios on reforming process efficiency and NH_3 conversion efficiency by reforming using exhaust gas before TWC.

The scale-up prediction for full scale application is based on the same NH_3 input energy density (table 2) as discussed in NH_3 direct decomposition results. The recovered fuel energy (Fig. 10 Left) increased as function of O_2/NH_3 ratio in the same trend as reforming process efficiency as shown in Fig. 9 (Left). The NH_3 -exhaust reforming at O_2/NH_3 ratio above 0.078 reveals the potential to recover more energy than direct NH_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_2/NH_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_2 .

On the other hand, the predicted value of gasoline saved and CO_2 reduced by utilising reformat 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_2 and NH_3 are taken into account and it is assumed that all H_2 and NH_3 fed into the engine will be converted into energy by combustion. As H_2 and NH_3 are CO_x -free species the amount of %fuel saved and % CO_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 reformat 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 reformat.

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 CO₂ emissions in comparison with the use of gasoline. When the on-board fuel reforming efficiency increment (30%) is taken into consideration, the reduction in CO₂ 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 CO₂ emissions can be expected.

Table 4 Summary of exergy and CO₂ footprint of fuel productions.

Fig.11 designation	Fuel	Energy cost (kJ/kJ)	CO₂ cost (gCO₂/MJ)	Reference
1A	NH ₃	1.85	94	[41]
2A	NH ₃	2.51	141	[42]
3A	NH ₃	1.40	0	[43]
4A	NH ₃	2.00	112	[44]
5A	NH ₃	1.35	76	[45]
6A	NH ₃	2.18	122	[46]
7A	NH ₃	1.55	87	[46]
8A	NH ₃	2.34	20	[47]
9A	NH ₃	4.20	45	[47]
10A	NH ₃	6.49	46	[47]
11A	NH ₃	8.55	18	[47]
12A	NH ₃	2.15	120	[48]
1G	Gasoline	1.22	81	[49]
2G	Gasoline	1.12	79.85	[50]
3G	Gasoline	1.10	75	[51]
4G	Gasoline	1.02	73	[52]
5G	Gasoline	1.31	87.01	[53]

6G	Gasoline	1.11	81.09	[54]
7G	Gasoline	1.97	123.91	[55]

Figure 11 Comparative amounts of CO₂ 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 NH₃ conversion for on-board H₂ production. This is through applying a promising and practical method using NH₃ which enables partial replacement of the gasoline fuel with on-board produced CO_x-free H₂. The performance evaluation of the NH₃ 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 CO₂ 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 emission 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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