



Using ammonia as a sustainable fuel

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ABSTRACT

In this study, ammonia is identified as a sustainable fuel for mobile and remote applications. Similar to hydrogen, ammonia is a synthetic product that can be obtained either from fossil fuels, biomass, or other renewable sources. Some advantages of ammonia with respect to hydrogen are less expensive cost per unit of stored energy, higher volumetric energy density that is comparable with that of gasoline, easier production, handling and distribution with the existent infrastructure, and better commercial viability. Here, the possible ways to use ammonia as a sustainable fuel in internal combustion engines and fuel-cells are discussed and analysed based on some thermodynamic performance models through efficiency and effectiveness parameters. The refrigeration effect of ammonia, which is another advantage, is also included in the efficiency calculations. The study suggests that the most efficient system is based on fuel-cells which provide simultaneously power, heating and cooling and its only exhaust consists of water and nitrogen. If the cooling effect is taken into consideration, the system's effectiveness reaches 46% implying that a medium size car ranges over 500 km with 50 l fuel at a cost below \$2 per 100 km. The cooling power represents about 7.2% from the engine power, being thus a valuable side benefit of ammonia's presence on-board.

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1. Introduction

Fossil fuels and their extensive use in various sectors, e.g., transportation, industrial, residential, commercial, etc. have caused some major problems for human health and welfare. To reduce the harmful effects of fossil fuels, some sustainable fuels and solutions need to be increasingly applied. One of the most important properties of sustainable sources is their environmental compatibility. This characteristic leads many to believe that sustainable fuels will become the most attractive energy sources in the short- and long-term future and be the most promising from technological and environmental perspectives through the current and future centuries, particularly in the context of sustainable development.

Even though hydrogen is recognized as a promising fuel, implementing a global hydrogen-based economy is at present a non-feasible approach unless a suitable storage medium could be found [1]. Furthermore, prohibitive investments are needed to develop a hydrogen distribution infrastructure which implies complicated safety issues because hydrogen is volatile and has a low flash point, presents explosion danger in air and its flame is invisible. Moreover, hydrogen has very low volumetric energy density

with respect to regular fuels used in transportation vehicles. Compared with gasoline this is four times less if hydrogen is stored in liquid state at $-235\text{ }^{\circ}\text{C}$ (this storage is not possible for long term on vehicles), or is 16 times less if hydrogen is stored at $25\text{ }^{\circ}\text{C}/200\text{ bar}$ pressure.

Ammonia's cost per volume of stored energy is three times less expensive than that of hydrogen [2]. Similar to hydrogen, ammonia can be used as a clean energy carrier and storage medium because ammonia can potentially be combusted in an environmentally benign way, exhausting only water and nitrogen [3].

The distribution infrastructure already exists for ammonia to deliver it in large amounts (approximately 100 million tons yearly [1]). Ammonia is stored in the same manner as propane, at 8 bar vapour pressure at room temperature. Moreover, the energy content of ammonia per unit of volume is comparable to that of gasoline which makes it a fuel attractive for transportation applications [4]. Furthermore, ammonia fuel has a narrow flammability range and therefore it is generally considered non-flammable when transported. If released into the atmosphere, ammonia's density is lighter than that of air and thus it dissipates rapidly. In addition, because of its characteristic smell the nose easily detects it in concentrations as low as $\sim 5\text{ ppm}$.

Due to these features ammonia is believed to be a key substance for the world future economy, including energy sector, transportation, refrigeration, agriculture, and other industries (e.g., ammonia is used as building block for the synthesis of many pharmaceuti-

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Nomenclature

COP	coefficient of performance
g	gas phase (in Eq. (6))
h	enthalpy (kJ kg^{-1})
HHV	higher heating value (MJ kg^{-1})
\dot{m}	mass flow rate (kg s^{-1})
T	temperature ($^{\circ}\text{C}$)
w	specific work (kJ kg^{-1})

Greek letters

ε	effectiveness (dimensionless)
η	efficiency (%)
λ	stoichiometric coefficient ($\text{kmol}_{\text{N}_2} \text{ kmol}_{\text{N}_3}^{-1}$)
μ	molecular mass (kg kmol^{-1})

Superscripts

"	vapour
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Subscripts

a	actual thermodynamic state
air	air
c	cooling effect
i	inlet of the turbine
in	inlet
NH_3	ammonia
Lc	low temperature cooling
out	outlet
r	refrigeration effect
s	isentropic
w	work recovered

cals and chemicals). Using ammonia as an energy carrier provides both a short and long term solution because ammonia can be synthesized either from fossil fuels (through gasification), from any kind of renewable energy, or from waste heat including that from nuclear reactors. Moreover, ammonia is fully recyclable because it can be made from water and nitrogen, substances available everywhere in the environment, and its combustion produces back the same amount of water and nitrogen.

The toxicity and flammability concerns of ammonia may be perceived as a challenge in its serious consideration for using as a sustainable fuel. However, such problems have largely been addressed and are compensated by well-established experience in ammonia handling, storage and use in various forms (i.e., gaseous, liquid as well as solid), especially in agriculture and refrigeration sectors.

Christensen et al. [5] suggested for the first time the idea of an ammonia-based economy in which fossil fuels are converted to ammonia and then ammonia used as a clean (synthetic) fuel in transportation and remote applications. Methods to produce ammonia from fossil fuels with simultaneous CO_2 sequestration are already mentioned in ref. [5], making thus the ammonia's life cycle CO_2 -neutral.

Ammonia can be absorbed in porous metal ammine complexes, e.g., hexaamminemagnesium chloride [6], $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ by passing ammonia over anhydrous magnesium chloride at room temperature and the absorption and desorption of ammonia is completely reversible. The ammine can be shaped in the desired form and can store 9% per weight (9 kg H_2 in 100 kg) and $100 \text{ kg H}_2 \text{ m}^{-3}$. This technique has been mentioned as a way to store ammonia on-board for vehicular applications and prevent thus any danger related to a crash.

Ammonia can be used directly as a fuel in alkaline [7] and solid oxide fuel-cells (SOFCs) [8] to produce steam and some NO_x as exhausts; the NO_x can be reduced by known methods. Moreover, direct ammonia solid electrolyte fuel-cells were recently developed.

In order to have ammonia as a fuel source for PEM fuel-cell vehicles, it is first cracked catalytically into nitrogen and hydrogen; this reaction is thermally driven by a $350\text{--}400^{\circ}\text{C}$ heat source [9]. This heat can be obtained by catalytic combustion of a small part of the generated hydrogen [10].

Compared with the methanol-reforming alternative, ammonia decomposition is more attractive, both from environmental and economical point of view: it is not emitting CO_2 ; there is no need to carry water for steam reforming; and the problem of PEMs electrodes poisoning with CO produced by the methanol reforming process is completely eliminated. As an alternative option, hydrogen can also be obtained via ammonia electrolysis [11]. This will definitely make it more cost effective, more commercially viable and reliable, and more environmentally benign than the hydrogen produced through some conventional techniques, e.g., obtaining hydrogen from natural gas.

Internal combustion engines (ICE) fuelled directly with ammonia must have special features because the ammonia's flame speed is too slow. Recent developments include homogeneous charge compression ignition (HCCI) technology that provides 40–50% efficiency [12] for a large range of compression ratios, i.e., 40:1–100:1, respectively. However, if decomposed first, ammonia can fuel regular internal combustion engines because the mixture of hydrogen, nitrogen, ammonia and air has combustion characteristics comparable to gasoline. Furthermore, possibilities exist to separate the hydrogen from nitrogen after decomposition [13] and thus to feed the cylinder with almost pure hydrogen; the combustion process is improved and NO_x emission minimized in this way.

This paper aims to discuss some potential options and advantages of using ammonia as a sustainable fuel in transportation vehicles. In the first section, ammonia is compared with other conventional fuels (e.g., gasoline, compressed natural gas (CNG), liquefied petroleum gas (LPG), methanol) as well as with hydrogen from the point of energy storage density per unit of volume and of mass, and the unitary cost per unit of storage tank volume. In the subsequent section the possibility of using ammonia simultaneously as a refrigerant is proposed and the refrigeration effect quantified in terms of refrigeration power vs engine's power. Furthermore, some types of power systems based on internal combustion engines and fuel-cells are investigated for performance comparison through thermal efficiency and effectiveness. We also study some more parameters, namely driving range and cost associated to 100 km driving range, for ammonia fuelled alternatives vs systems powered with other fuels for comparison purposes.

2. Ammonia fuel vs other fuels

As a first step in analyzing the features of ammonia as a sustainable transportation fuel, a comparison with other fuel alternatives should be made in terms of energy stored per unit of mass or volume, and of cost per unit of storage tank volume. The most relevant features of some major fuels together with the ammonia's characteristics are summarized in Table 1. The higher heating value is indicated to cope with the current trend toward cleaner fuels that can be exhausted at lower temperature.

Table 1 lists the fuel and the type of storage in the first column, the fuel pressure in the tank, the fuel density in the full tank (except

Table 1
Comparison of ammonia with other fuels and hydrogen

Fuel/storage	P (bar)	Density (kg m^{-3})	HHV (MJ kg^{-1})	Energy density (GJ m^{-3})	Specific volumetric cost ($\text{\$ m}^{-3}$)	Specific energetic cost ($\text{\$ GJ}^{-1}$)
Gasoline, C_8H_{18} /liquid tank	1	736	46.7	34.4	1000	29.1
CNG, CH_4 /integrated storage system	250	188	55.5	10.4	400	38.3
LPG, C_3H_8 /pressurized tank	14	388	48.9	19.0	542	28.5
Methanol, CH_3OH /liquid tank	1	749	15.2	11.4	693	60.9
Hydrogen, H_2 /metal hydrides	14	25	142	3.6	125	35.2
Ammonia/pressurized tank	10	603	22.5	13.6	181	13.3
Ammonia, NH_3 /metal amines	1	610	17.1	10.4	183	17.5

for gasoline and methanol where the density refers to the liquid itself). Other listed characteristics are the higher heating value, the energy and exergy densities, the specific volumetric cost (given with respect to the internal volume of the tank), and the specific energetic cost (given in terms of cost per unit of energy).

Based on the results listed in Table 1, we now discuss the fuels and compare them for the energy, performance, thermodynamic parameters, etc.

- **Gasoline** represents the reference fuel in our analysis. It is obtained via distillation of crude oil in refineries, which is a relatively expensive process aimed at eliminating various toxic components such as lead, sulphur, etc. The fuel's specific energetic cost is high, i.e., about $29 \text{\$/GJ}$ (Table 1). Compared to other fuels, gasoline packs the most energy per unit of volume. Apart from its high specific cost, when combusted in an ICE, gasoline emits SO_x , NO_x and large amounts of CO_2 and other pollutants.
- **Compressed natural gas** CNG represents a cleaner alternative to gasoline having the advantage of lower CO_2 emissions; no SO_x are exhausted. Typically, CNG is stored under 250 bar pressure on special "integrated storage systems" in cars; this system consists of a number of tubular tanks interconnected to each other and embedded in safety foam to avoid fracture danger during a crash. Because of its gaseous phase the energy density stored in the CNG tank is more than three times lower than that of gasoline. This fact leads to an expensive specific energy ($38 \text{\$/GJ}^{-1}$) even though the cost of a full tank is 2–3 times cheaper than the same volume of gasoline. However, the CNG engine runs more efficiently and therefore the cost per 100 km drive is slightly superior to that of gasoline car.
- **Liquid petroleum gas** LPG is stored in pressurised canisters at 14 bar in thermodynamic equilibrium with its vapours. The energetic value of LPG is about the same as that of gasoline, but the LPG tank packs three times less energy. Similarly to the CNG, the advantage of LPG consists in its lower emissions and the higher engine efficiency. LPG consists mainly in propane, while CNG in methane. Thus, these fuels being almost pure chemical substances can be combusted in a clean way; on the contrary, gasoline being a complex blend that contains toxic components, obtaining a clean exhaust is more expensive from both investment and operating costs points of view.
- **Methanol** is considered a potential option for fuel-cell cars; after steam reforming, methanol is converted to hydrogen. Considering this fact, in Table 1 the higher heating value (HHV) of methanol has been diminished with the energy necessary for reforming. The energy density of methanol is three times less than that of gasoline, but the fuel cost per unit of tank volume is double.
- **Hydrogen** is attractive for its high heating value and its clean combustion which produces only water. However, it is difficult to store hydrogen on board of vehicles. The state of the art systems store hydrogen in metal hydrides under densities up to 25kg m^{-3} and pressures of about 14 bar. Hydrogen is produced either from fossil

fuels or renewable sources. Whatever is the method of production (electrolysis, gasification, etc.) the cost of hydrogen is relatively high (over $5 \text{\$/kg}$ or $35 \text{\$/GJ}^{-1}$) mainly because of the cost of compression and separation (especially when it is produced from syngas). Moreover, the volumetric density of the storage tank being the lowest (3.6GJ m^{-3}) the driving range of the hydrogen vehicle is affected mostly, even though the current fuel-cell vehicles tend to be very efficient.

- **Ammonia** is proposed as a potential fuel which can be cheaply produced from syngas via the well established Haber–Bosh process. By adding nitrogen to syngas ammonia is formed over catalysts and then separated with no energy penalty via condensation. In general, the primary material to produce ammonia is methane, but any other fossil fuels or biomass can also be used. Furthermore, ammonia can be produced in a biological way from manure and waste by special micro-organisms. It is interesting to remark that the cost of energy in form of ammonia is only $13.3 \text{\$/GJ}^{-1}$ as compared to $38.3 \text{\$/GJ}^{-1}$ for CNG which contains mostly methane. In fact, methane is the feedstock to produce ammonia in industry. This aspect is explained by the large costs associated to methane's on-board storage in a compressed state.

One may see a drawback in ammonia for its storage in the passenger vehicles due to the toxicity problem. In a car crash, ammonia liquid may leak and become harmful to living species. This obstacle can be overcome by innovative ways of ammonia storage. One possibility is to embed ammonia in metal amines, as mentioned in the introduction. Doing so, the danger of toxicity is completely eliminated because ammonia can be released only by heating the porous media at 350°C or more. The energetic drawback of this system comes from the energy needed for ammonia release that leads to a cost increase to $17.5 \text{\$/GJ}^{-1}$.

The results discussed in this section are summarized graphically in Fig. 1 which illustrates the volumetric energy density vs the gravimetric energy density stored on-board on various fuels. The storage system corresponds to the one mentioned in Table 1.

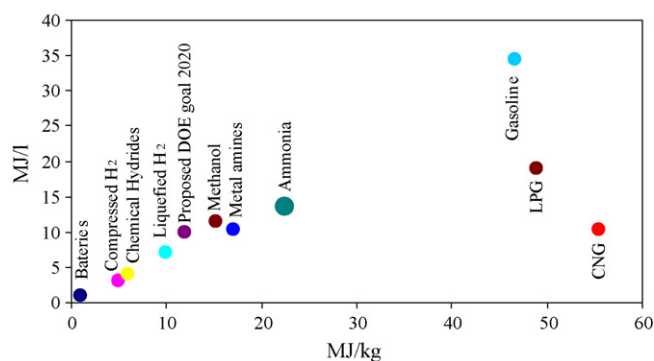


Fig. 1. Comparison of volumetric and gravimetric energy densities of various fuels.

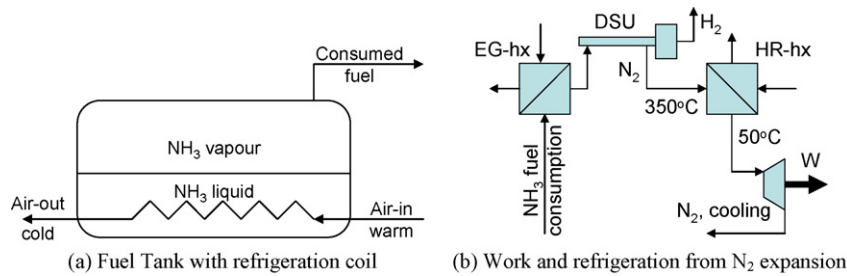


Fig. 2. Ways of exploiting the refrigeration effect of NH_3 -fuel on-board DSU – decomposition and separation unit, EG-hx – exhaust gases heat exchanger, HR-hx – heat recovery heat exchanger, W – work recovery from turbine.

3. A novel approach to use on-board ammonia for cooling

Storing liquid ammonia on-board has an important advantage that should not be neglected: it can be used for cooling needs. Two ways of exploiting the refrigeration effect of ammonia fuel on-board are presented next.

Assume that ammonia vapour is extracted from the pressurized tank at a certain temperature. While leaving the tank, the vapour take-out their flow enthalpy. This enthalpy is replaced by evaporation of the corresponding quantity of liquid. Both the temperature and the pressure in the tank decrease in this way. If a cooling coil is embedded into the liquid, then the temperature and pressure in the tank can be stabilized at a desired temperature. In this way the cooling effect induced by the ammonia vapours extraction from the tank is exploited.

Consider the configuration illustrated in Fig. 2(a) and note T the equilibrium temperature in the tank. Then the energy rate (i.e., power) balance is written as follows:

$$h''(T)\dot{m}_{\text{NH}_3} = \dot{m}_{\text{air}}(h_{\text{in}} - h_{\text{out}}) \quad (1)$$

where the LHS parameters refer to the enthalpy and flow rate of ammonia vapour and the RHS parameters refer to air entering and leaving the system; the air is cooled in this way for air-conditioning purpose. The effectiveness of the cooling effect can be quantified as a fraction of the HHV of ammonia below:

$$\varepsilon_c = \frac{h''(T)}{\text{HHV}} \quad (2)$$

To give an example, if one assumes $T = 15^\circ\text{C}$, the specific enthalpy of the vapour at this condition is 1.62 MJ kg^{-1} which represents 7.2% from the HHV of ammonia. It is to be mentioned that the simplicity of this air conditioning system lowers both the initial, operation and maintenance costs by eliminating the conventional mechanical air-conditioning system.

Furthermore, additional low-temperature cooling, and heat and work recovery can be obtained from the exhausted nitrogen stream. One possibility to do this is illustrated in Fig. 2(b) that illustrates the process of H_2 production from ammonia by thermal decomposition and separation. The ammonia fuel vapours are preheated in an exhaust gas heat exchanger (EG-hx) with some heat generated on-board via hydrogen combustion. The temperature level corresponding to ammonia's thermal decomposition is about 350°C . Ammonia is directed toward the decomposition and separation unit (DSU) that produces the hydrogen and nitrogen. The stream of nitrogen is cooled in the heat-recovery heat exchanger (HR-hx) at a temperature close to ambient, assuming 50°C . Then, the nitrogen is expanded in a turbine for work recovery. The resulted cold stream of nitrogen can be used for some low-temperature cooling needs before being exhausted out to the atmosphere. Calculating this additional cooling effect and the corresponding work recovery can be made by assuming an isentropic efficiency of the turbine, η_s , and computing the actual expansion enthalpy h_{a,N_2} as function

of the N_2 inlet enthalpy, h_i :

$$h_{a,\text{N}_2} = h_{s,\text{N}_2} + \eta_s(h_{s,\text{N}_2} - h_i) \quad (3)$$

where h_i is calculated at the decomposition temperature and pressure (up-stream turbine), and the isentropic discharge temperature, h_{s,N_2} is calculated with the up-stream entropy and discharge pressure.

It is useful to report the recovered work in terms of energy per kilograms of consumed ammonia fuel as follows (this can be done by taking into account the number $\lambda = 0.5 \text{ kmol}_{\text{N}_2} \text{ kmol}_{\text{NH}_3}^{-1}$ resulting from the NH_3 decomposition equation $\text{NH}_3 \rightarrow 1.5\text{H}_2 + \lambda\text{N}_2$):

$$\Delta h_w = \lambda \frac{\mu_{\text{N}_2}}{\mu_{\text{NH}_3}} (h_{a,\text{N}_2} - h_i) \quad (4)$$

The additional low-temperature cooling effect of N_2 can be quantified by considering re-heating of the nitrogen stream from its low temperature T_{a,N_2} to a temperature close to ambient, T_0 , featuring the flow enthalpy h_{0,N_2} :

$$\Delta h_{\text{LC}} = \lambda \frac{\mu_{\text{N}_2}}{\mu_{\text{NH}_3}} (h_{0,\text{N}_2} - h_{a,\text{N}_2}) \quad (5)$$

The effectiveness calculated with respect to work $\varepsilon_w = \Delta h_w / \text{HHV}$ and cooling ε_{LC} , $\varepsilon_{\text{LC}} = \Delta h_{\text{LC}} / \text{HHV}$ effects is summarized in Table 2, which also includes a comparison with LPG (propane). Similarly to ammonia, LPG is stored in equilibrium with its vapours. Therefore, a cooling effect can be exploited in the way illustrated by a system such as that depicted in Fig. 2(a). Note that the LPG and NH_3 can be compared, as indicated in Table 2, only with respect to the parameter ε_c .

For obtaining the results listed in Table 2, a temperature of 15°C is assumed in the tank, temperature which corresponds to a vapour pressure of about 7.3 bar for both LPG and NH_3 , and the isentropic efficiency of the turbine considered is 80% as a typical value.

According to the results obtained from Table 2 on a 70 kW engine fuelled with propane, a 0.84 kW of refrigeration can be obtained. In contrast, for a similar power fuelled with ammonia the delivered cooling is 5 kW. Assuming a COP of 2, this figure means 2.5 kW saved from the shaft torque if ammonia refrigeration effect is used instead of a mechanical air conditioner. Furthermore, assuming a rapid cooling of a 4 m^3 cabin with 325 air changes per hour in summer conditions at 30°C outside temperature, Eq. (1) can be solved for the inside air temperature and it results a value of 18°C that is very satisfactory for comfort needs. Additionally, the system will produce 700 W low-temperature cooling from expanded nitrogen, and recover 280 W turbine shaft work.

Table 2
Refrigeration and work recovery from ammonia and LPG

Fuel	ε_c (%)	T_{a,N_2} ($^\circ\text{C}$)	ε_w (%)	ε_{LC} (%)
Ammonia	7.2	-51.8	0.4	1
LPG	1.2	-	-	-

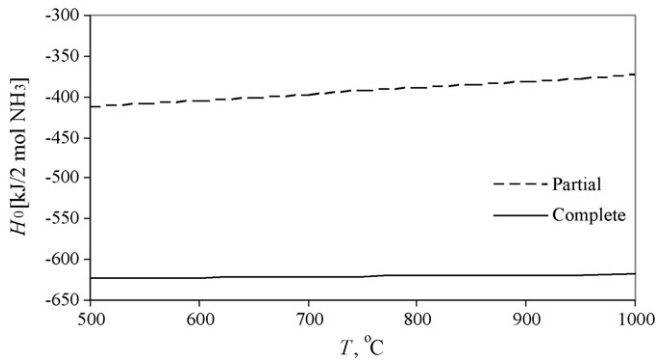
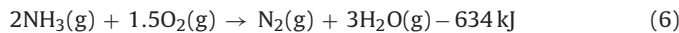


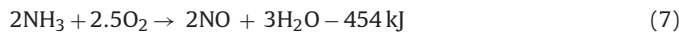
Fig. 3. Partial oxidation vs complete oxidation during the anodic reaction.

4. Performance analysis

When ammonia is used as a fuel in any combustion system or a fuel-cell, the desired chemical reaction is the complete oxidation that produces only steam and nitrogen and some considerable amount of heat, according to the equation given below:



However, in most of the practical situations the reaction kinetics are favourable to nitric oxide formation. Thus, the partial oxidation of ammonia occurs normally as



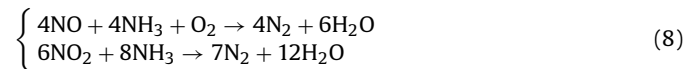
The reaction heats in Eqs. (6) and (7) are indicated only for order of magnitude estimation in standard conditions (25 °C, 1 atm). Considering the operating range of high temperature fuel-cells and of ICEs in terms of temperature, i.e., 500–1000 °C, the reaction heat contents for partial and complete oxidation cases are calculated using the equations, correlations and data given in NIST Chemistry WebBook [16]. The results obtained in terms of reaction heat vs process temperature are shown in Fig. 3. From Fig. 3 it can be inferred

that the partial oxidation of ammonia reduces the useful reaction heat by 33% and moreover the reaction heat dependence on the temperature is more profound than in the case of complete oxidation, therefore it potentially induces problems with the process control.

In order to minimize the partial ammonia oxidation, ammonia must be cracked first, according to the endothermic reaction $2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2 + 94 \text{ kJ}$. SOFC and ICE's present an advantage in this respect due to their high operating temperatures at which ammonia can be decomposed thermally over catalysts. Keeping this aspect in mind, let us consider some possible power systems with NH_3 . There are, as can be seen from Fig. 4, two main approaches that are applicable to ammonia fuelled power generation in transportation vehicles, namely ICEs and fuel-cell systems.

Considering the first case, the ICEs, ammonia can directly be used as a fuel in HCCI engine of the type mentioned in the introduction. Typically, a compression ratio in the order of 50:1 is used in such engines. As previously indicated, some high thermal efficiencies, based on the first law of thermodynamics, accounting for over 40% are obtained.

Moreover, the advantage of having ammonia on-board allows for subsequent reduction of the NO_x formed during ammonia's combustion, according to the following reactions, conducted catalytically over zeolites:



Here, reactions given above reveal that, if ammonia's combustion is incomplete (reaction (7)) for every mole of fuel consumed for combustion there is a need of another mole for NO_x reduction. In such conditions, the driving range of a zero- NO_x emission vehicle is reduced to a half with respect to NO_x -emitting one. However, if enough cooling is applied and the combustion temperature is maintained to lower levels, then the incomplete combustion can be minimized in favour of the complete oxidation. The NO_x emissions can be assumed in general as being similar to the levels specific to gasoline engines, namely [14] 10^{-2} mol

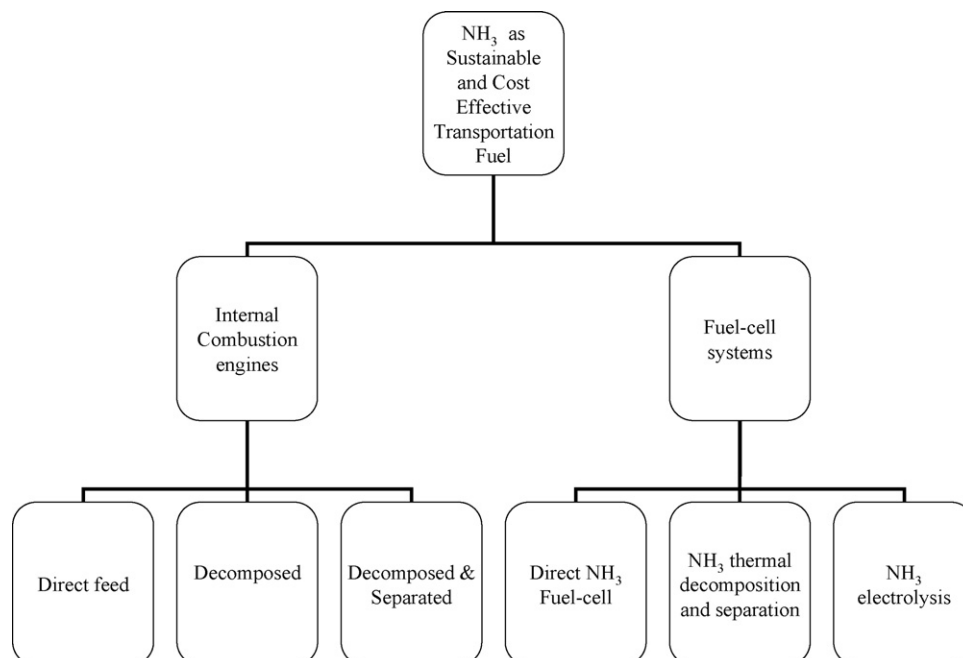


Fig. 4. Possible power systems fuelled with ammonia.

NO mol NH_3^{-1} . To reduce these emissions based on the reactions given in Eq. (8) stoichiometry, an extra 6 ml of ammonia is needed for every 200 km, which represents an insignificant quantity.

When estimating the engine performance the cooling effect should be taken into account. In order to derive an engine effectiveness that includes the cooling effect, let us consider η as the engine efficiency. We need to assume a typical COP of a mechanical air-conditioning system (e.g., 2 for automobiles) and ε_c to be calculated from Eq. (2). The equivalent work needed for a mechanical cooling system then becomes

$$w_r = \frac{\varepsilon_c \text{HHV}}{\text{COP}} \quad (9)$$

Using this, the effectiveness of the ammonia ICE including the cooling effect is

$$\varepsilon_r = \frac{w + w_r}{\text{HHV}} = \varepsilon + \frac{\varepsilon_c}{\text{COP}} \quad (10)$$

For the direct ammonia system considered here, the second term in Eq. (10) may have a value of 3.6% (see Table 2), therefore, resulting in an equivalent efficiency of the system of 44%.

Another option for ICEs may be the decomposition of ammonia first, and then fuelling a regular engine with a mixture of hydrogen, nitrogen and small traces of non-decomposed ammonia, respectively. A limited quantity of NO_x may be formed due to the presence of nitrogen in the combustion chamber where hydrogen is mainly combusted. However, the presence of ammonia in the combustion chamber forces reactions in Eq. (8) to occur, and this reduces the amounts of emitted NO_x even more. Here, let us assume an energy efficiency of 24% as similar to gasoline engine and see how much an improved effect of cooling takes place. We can call this an efficiency upgrade as $24\% + 3.6\%$ due to cooling effect (see Eq. (10)) which becomes 27.6%. Of course, if one considers an energy efficiency of 27%, the overall efficiency (with cooling effect) then becomes more than 30.6%. This shows that there is a potential for performance improvement of vehicles. If one concerns about NO_x , the amount of NH_3 used for NO_x reduction as an agent is considered negligible.

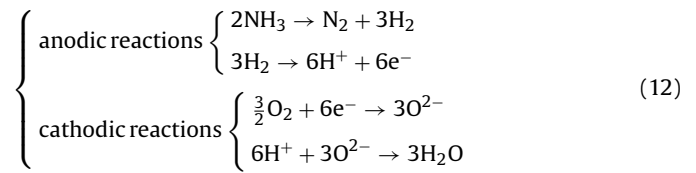
The third ICE option consists in using a decomposition and separation unit, as illustrated in Fig. 2(b). In this case, the efficiency of 24% is upgraded according to

$$\varepsilon_r = \varepsilon + \frac{\varepsilon_c}{\text{COP}} + \varepsilon_w. \quad (11)$$

In determining ε_w it is assumed that the nitrogen is expanded immediately after the DSU (see Fig. 2(b)), i.e., the heat recovery heat exchanger is eliminated. In doing so we obtain an efficiency increase by 0.7% (from the fuel HHV) as a result of shaft work recovered and by another 0.4% due to the heating (while a stream of nitrogen at 157°C is still available for satisfying heating needs) and ends up with an efficiency improvement of 1.1%. If we add up this to the conservative figure (i.e., 27.6%), it becomes 28.7%, respectively. If we add it up to 30.6%, it becomes 31.7%, respectively. These are of course key advantages of this kind arrangement for ammonia in practice.

Let us consider now the fuel-cell approaches. First, one analyses direct ammonia fuel-cell systems. Dedicated, so-called direct ammonia fuel-cells have been recently developed. For example, Maffei et al. [15] developed recently a direct ammonia fuel-cell that additionally to the anodic decomposition uses a proton conducting solid electrolyte. Therefore, the protons migrate over the solid electrolyte and reach the cathode where the water formation reaction occurs. At the anode, the nitrogen obtained via ammonia decomposition remains unreacted and is delivered out as a hot stream. The

complete set of reactions of this kind of solid electrolyte ammonia fuel-cell is as follows (e.g., ref. [15]):



The solid electrolyte ammonia fuel-cells operate at high temperatures between 500°C and 1000°C and may attain efficiencies as high as 55%. However, considering the overall system an efficiency of 40% is achievable; including the cooling effect the possible efficiency may reach about 44%, respectively.

It should be noted that in such systems, the efficiency is affected by the anode/electrolyte temperature in such a way that a temperature drop of 100°C degrades the power density by about 66%. Therefore, an accurate control of the system must be managed to keep the cell working at optimum conditions. If ammonia is decomposed and hence separated, then hydrogen can be fuelled directly to a high performance fuel-cell and the nitrogen expanded for work and low temperature cooling. If one assumes a system efficiency of 40%, by accounting for the cooling and work recovery, one can go further up to 46%.

The last option may be the use of an ammonia electrolyser coupled with a proton exchange membrane fuel-cell. From what the current literature [14,15] say regarding ammonia electrolysis, it is clear that the theoretical conversion efficiency is extremely high. However, due to the difficulty in catalyst optimization the current technology may not allow for higher efficiencies. An efficiency of 20%, including the refrigeration and work recovery effects, is therefore obtained [11]. It is expected that the electrolysis technology of ammonia will evolve and make this technique a real choice for on-board generation of hydrogen from NH_3 .

Furthermore, a total of six approaches as summarized in Fig. 4 are compared in Table 3 with other systems, including the conventional gasoline vehicle. In the same table, there are also indicated the effectiveness of the system ε_r (including the refrigeration and work recovery wherever possible), the fuel cost per 100 km, and the driving range. Note that a value of 0.5 MJ km^{-1} shaft work to drive a medium size vehicle has been used for calculating the results as presented in Table 3.

It is significant to assess the influence of the cooling effect on the effectiveness of the ammonia engine as a function of the ammonia's saturation temperature T in the fuel tank. A practical range for T is taken as $0\text{--}20^\circ\text{C}$. Finally, Fig. 5 shows how the quantity $\varepsilon_r(T)/\eta$ changes with evaporator temperature at three different efficiencies of the ammonia engine. The results reveal that the engine's effectiveness is superior with 10–20% of the efficiency, due to the presence of ammonia cooling.

Table 3
Performance of ammonia power systems and of other systems

Fuel/system	ε_r (%)	$\$ 100 \text{ km}^{-1}$	Range (km)
Gasoline/ICE	24	6.06	825
CNG/ICE	28	6.84	292
LPG/ICE	28	5.10	531
Methanol/reforming + fuel-cell	33	9.22	376
H_2 metal hydrides/fuel-cell	40	4.40	142
NH_3 /direct ICE	44	1.57	592
NH_3 /Th decomp, ICE	28	2.38	380
NH_3 /Th decomp Sep, ICE	31	2.15	420
NH_3 /direct FC	44	1.52	597
NH_3 /Th. decomp + Sep, FC	46	1.45	624
NH_3 /electrolysis	20	3.33	271

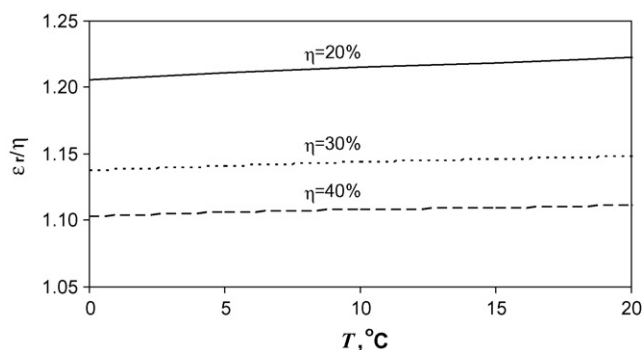


Fig. 5. Increment of the engine effectiveness due to the cooling effect of ammonia at various evaporating temperatures.

5. Conclusions

In this paper, we have investigated the use of ammonia in ICES and ammonia fuel-cells as a sustainable fuel as well as for hydrogen production for PEM fuel-cells and compared with other conventional fuels (gasoline, compressed natural gas (CNG), liquefied petroleum gas (LPG), methanol) as well as with hydrogen from the points of energy storage density per unit of volume and of mass, and the unitary cost per unit of storage tank volume. We have also proposed the option of using ammonia simultaneously as a refrigerant for cooling effect as quantified in terms of refrigeration power vs engine's power. A performance investigation of the above said options was performed for comparison purposes through their energy efficiencies and effectiveness, along with a study of some additional parameters, such as driving range and cost associated to 100 km driving range, for ammonia fuelled alternatives vs systems powered with other fuels. Here are some concluding remarks as drawn from this study:

- Ammonia is the least expensive fuel in terms of $\$GJ^{-1}$.
- In terms of $GJ m^{-3}$ ammonia becomes the third, after gasoline and LPG.
- There is an advantage of by-product refrigeration, 7.2% from HHV, which reduces the costs and maintenance.

- Ammonia is the cheapest fuel per 100 km driving range as a reasonable and practical assumption.
- Some additional advantages of ammonia are commercial availability and viability, global distribution network, easy handling experience, etc., while its toxicity may be seen as a challenge. This can easily be overcome with the current control and storage technologies.

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