



HAL
open science

Ammonia as Fuel for Transportation to Mitigate Zero Carbon Impact

Christine Mounaïm-Rousselle, Pierre Bréquigny, Agustin Valera-Medina,
Elena Boulet, David Emberson, Terese Løvås

► **To cite this version:**

Christine Mounaïm-Rousselle, Pierre Bréquigny, Agustin Valera-Medina, Elena Boulet, David Emberson, et al.. Ammonia as Fuel for Transportation to Mitigate Zero Carbon Impact. Gautam Kalghatgi; Avinash Kumar Agarwal; Felix Leach; Kelly Senecal. Engines and Fuels for Future Transport, Springer Singapore, pp.257-279, 2022, Energy, Environment, and Sustainability, 978-981-16-8719-8. 10.1007/978-981-16-8717-4_11 . hal-03501644

HAL Id: hal-03501644

<https://hal.science/hal-03501644>

Submitted on 23 Dec 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Ammonia as fuel for piston engines to mitigate zero carbon impact

Christine Mounaïm-Rousselle¹, Pierre Bréquigny¹, Agustin Valera Medina², Elena Boulet², David Emberson³, Terese Løvås³

¹Univ. Orléans, INSA-CVL, PRISME, EA 4229, F45072, Orléans, France

²College of Physical Sciences and Engineering, Cardiff University, Cardiff, UK

³ Department of Energy and Process Engineering, Norway University of Science and Technology, Trondheim, Torgarden, Norway
christine.rousselle@univ-orleans.fr

Abstract. The idea of using ammonia as a fuel is nothing new as its first well-known use was accomplished in buses within a Belgian fleet during World War II. Although several studies performed during the mid-60's investigated the possibility to consider ammonia as fuel for internal combustion engines (mainly by means of CFR experiments or 0D modelling), ammonia-based combustion engine fueling methods were not ready to be marketed as the use of this toxic molecule still poses major challenges - not only because of its supply and associated safety issues, but also because of its physical characteristics compared to conventional fossil fuels. As a function of the target to supply ammonia either partially in standard engines to limit carbon footprint or to employ it mainly in dedicated engines to reach zero footprint, the technological challenges in dual or sole fuel injection, either in SI or CI engines, could vary if the molecule is used as a source for main power or for auxiliary power units (ie. to extend the range of battery vehicles). Its use would also be a function of the transportation type (medium duty or heavy duty engines for freight, construction, marine transportation, etc.), hence creating a complex scenario. In this chapter new results of advanced researches will be discussed in order to highlight the potential of this future green fuel in internal combustion engines.

Keywords: ammonia, internal combustion engine.

1 Introduction

To reach the carbon neutrality target of 2050, many governments decided to consider clean and intermittent renewable energy resources (such as wind and solar) as main energy resources. However, due to the intermittency of these sources not being in phase with the demand, thus suffering to keep a secure electricity supply, energy storage has

been considered as an integral part of modern electricity smart grids to ensure continuous supply. One way to store renewable energy excess is via water electrolysis to produce hydrogen. Hydrogen can be used to fill any energy converters for electricity, industry or transportation purposes. Whilst the technologies are making great leaps forward, until now the transportation of hydrogen includes its liquefaction (at -253°C) by employing large scale plants, or through its compression at high pressures (up to 700 bar). Therefore, other alternatives have been presented over the years. One of these alternatives for hydrogen carriers is ammonia, which has some advantages over hydrogen due to its lower cost per unit of stored energy, its higher volumetric energy density, easier and more widespread production, handling and distribution capacity, and better commercial viability. Furthermore, its liquid phase can be achieved by compression to only 0.9 MPa at atmospheric temperature; these attributes have enabled a well-established, reliable infrastructure that has been developed over decades and that exists for both ammonia storage and distribution (including pipeline, rail, road, ship), as underlined by Valera-Medina et al. in their accurate and comprehensive recent review [1]. Ammonia also has the potential to be an energy carrier in its own right, as it can be used directly in high temperature fuel cells, gas turbines and piston engines. It is important to emphasize that ammonia is *complementary* to the delivery of the “Hydrogen Economy”, and will participate to reach full decarbonization targets especially for heavy duty, off highway and marine engines to address the transport and storage problems. Recent studies based on global system analyses are convinced that ‘green’ ammonia has a real potential to be considered as an electro-fuel candidate with greenhouse gas emissions from an ammonia-driven vehicle lower than one third of gasoline- or diesel-driven vehicles [2-4] Moreover, since the International Maritime Organization clarified its strategic roadmap to fully decarbonize this sector as soon as possible, ammonia has been considered as a real candidate to reach these targets. Moreover, over the last 10 years, the potential of partial use of ammonia for stationary power units has started to be explored with various demonstrators around the planet, hence denoting the potential of this molecule.

1.1 A brief history of ammonia fuel

Even though at the moment there is no ship or any transport fleet operating with ammonia as a fuel, the idea of using ammonia for transportation vehicles is not so recent, with a story that started early during the 20th century as recently well summarized in [5]. Briefly, after some examples experienced during the 30s/40s, the conversion of a truck by Norsk Hydro and a bus fleet by a Belgian public company during World War II demonstrated the potential of using ammonia as a fueling source [6]. 20 years later, several US studies considered the possibility of using ammonia as a fuel, but only experimental applications or isolated vehicle tests were carried during this period. In 1972, the first ammonia-fueled urban vehicle built at The University of Tennessee competed in the Urban Vehicle Design Competition [7]. This development would be followed by other small ventures where American institutions would travel the country to show the potential of ammonia [8], point at which the technology would halt for dec-

ades. It would be during the 2010s that several retrofitted initiatives would be attempted to demonstrate how ammonia can be used as fuel in combination with gasoline or diesel as depicted in [9]. These works would lead to several intellectual property outcomes, including one patent from Toyota recently filed [10] and some novel NH₃-fueled cars tested during 2010-15s (ie. AmVeh, Eco Explorer Marangoni Toyota or NH₃ car projects) as underlined in [5] and summarized in Figure 1.

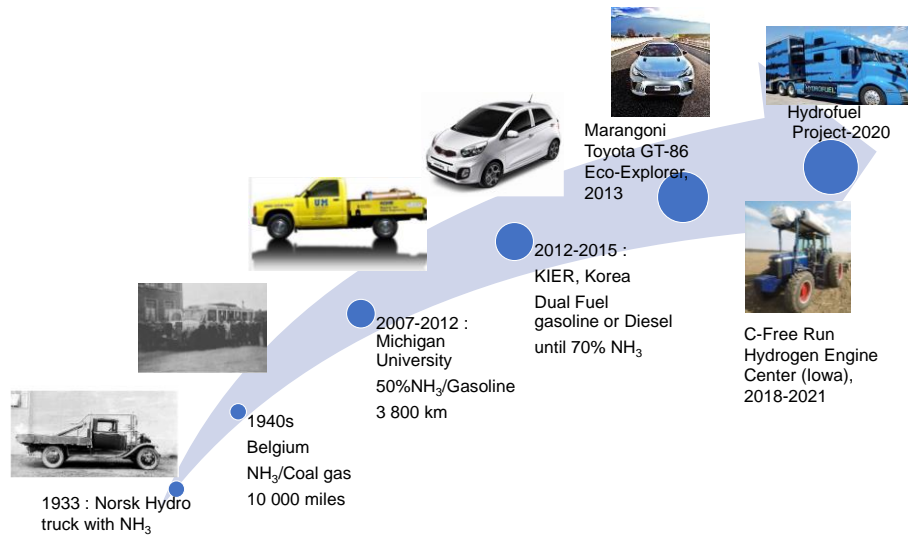
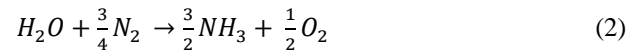
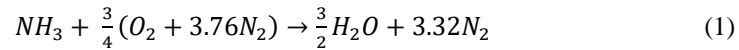


Fig. 1. Summary of NH₃ vehicles

1.2 Ammonia properties and specifications

The one-step oxidation reaction of NH₃ is very simple as in (1). If one considers the direct production pathway through water electrolysis as in (2), considering the global cycle, ammonia combustion is very attractive as from its production from water & air, this water & air is in turn recovered after passing through an energy conversion system. Of course, there are process yields and losses at different stages, but without any carbon-type emissions.



But before considering ammonia as a fuel, its main combustion characteristics need to be introduced as summarized in Table 1.

Table 1. Ammonia combustion properties
 (* for stoichiometric mixture, not real emissions).

Fuel	Ammonia	Hydrogen	Methane	Gasoline	Diesel
Molar mass (g/mol)	17	2	16	114	167
Heat Capacity Ratio	1.32	1.41	1.32	1.4	1.4
Flammability limit (% vol.)	15.8%-28%	4% - 76%	4.4%-17%	1.4% - 7.6%	1% - 6%
Octane Number	>130	>100	130	87-93	0
Auto-ignition temperature (°C)	651	530	537	440	225
stoich. Air/fuel ratio (mass)	6	34.3	17.1	15	14.6
Lower heating value (MJ/Kg fuel)	18.8	120	50.1	42.5	45
Energy content at stoich. (MJ/kg air)	3.13	3.5	2.92	2.83	3.08
% CO ₂ emitted by stoich. Combustion	0	0	9.5	12.5	12.6*
Laminar flame speed at Patm, 100°C (m/s)	0.12	35	0.38	0.42	

Ammonia's very narrow flammability limits in comparison to hydrogen can be considered an advantage as it poses much less explosive risks. However, due to an issue associated with high auto-ignition temperature (ie. 1.5 that of gasoline and 3 of diesel fuel), ammonia has implications on ignition occurrence in internal combustion engines, whether the ignition types are by spark or compression. Therefore, additional fuels and high compression ratios to promote ignition need to be considered to enhance both ignition delay time and auto-ignition temperature. The laminar flame speed of ammonia is the lowest among most conventional fuels, inducing a very slow combustion process. Hence, the reaction rates are slow, which is typically not desired for an IC engine application as only a fraction of the injected fuel mixture would be burned, thus leading to inefficiencies and instabilities of the combustion process. This characteristic of ammonia also limits the engine operation at high regime conditions. The flame quenching distance for ammonia/air is 7 mm at stoichiometric conditions, about 10 times that of hydrogen. This also implies that the heat losses from the flame to the wall will be less in the case of ammonia. Further, the lower heating value of ammonia is less than half of that of typical engine fossil fuels. However, the stoichiometric air/fuel ratio for ammonia is also about half of that of typical fuels. This means that for the same amount of intake air, the input energy quantity will be similar, but with double the fuel consumption. Interestingly, the adiabatic flame temperature from ammonia combustion is around 1800 K (somewhat low), which is high enough to extract work.

Ammonia is unlikely to cause engine knock under regular combustion engine conditions, but as recently indicated in Mounaïm-Rousselle et al. [10, 11,12] enhancing the engine optimization for spark ignited ammonia combustion might lead ammonia engines to operate at high compression ratios or high boosting pressures. Under these conditions, the physical conditions of the system and the engine knock can be relevant. The real Octane Number of ammonia is unknown but has been estimated at ~130 [12] which is very high, hence knock is unlikely to happen. This property of ammonia would allow using various means to improve engine efficiency, such as increasing the compression ratio or use supercharging or turbocharging without risking knock [13, 14]. Further, the heat of vaporization of ammonia is very high (1370 kJ/kg [15]) in comparison to gasoline (between 180-350 kJ/kg). This is one reason why ammonia is commonly used as a refrigerant. This is another advantage regarding spontaneous ignition. However, the induced reduction of in-cylinder temperature could lead to misfires and

restrict the range of operating conditions in the case of direct liquid injection, a concept still under research scrutiny.

As most of its properties seem to indicate, pure ammonia fuel would be knock resistant, denoting low flame speed and, in the case of direct liquid injection, having a high heat of vaporization, therefore making stable combustion hard to achieve.

Latest research has shown that using ammonia blends helped overcome all these issues, enabling ammonia as a suitable candidate for carbon-free fueling applications for classical engine architectures (ie. Spark-Ignition (SI) and Compression Ignition (CI)) as reviewed in [1, 10, 16]. The blend of ammonia with gasoline, diesel fuel or other more usual fuels for engines can allow greater fuel flexibility. However, and as schematized in Figure 2, in order to consider ammonia as a real carbon-free fuel, only filling the engine with pure ammonia or blended with hydrogen (on board if possible) will be the unique way to avoid CO₂ emissions.

The chapter will be divided into 5 sections: the first will review the latest research of SI engines fueled with ammonia whilst identifying several trends; the second chapter will focus on CI engines; the third will be dedicated to an advanced combustion mode for low emissions engines, i.e. homogeneous combustion compression ignition engines; the fourth will highlight the difficulties in getting a range of wide-operating conditions especially related to cold start operations. Finally, the last section will summarize the emission problematics when employing ammonia fuel.

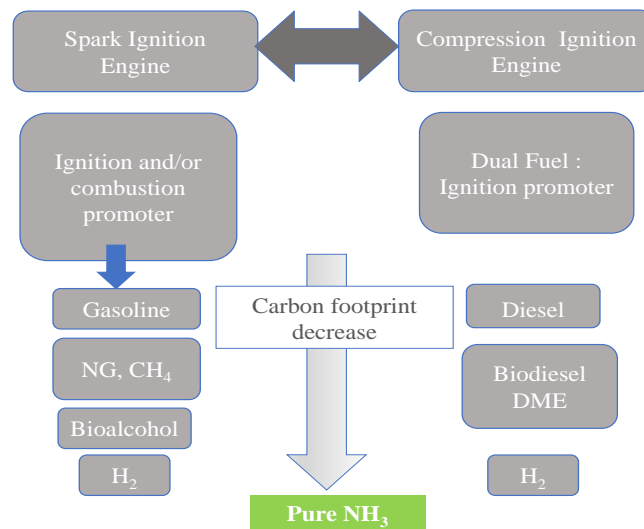


Fig. 2. Different technologies paths to use using ammonia as fuel for ICE

2 Ammonia SI engine

Different practical methods for improving engine performance while burning ammonia (ie. increase spark energy, increase compression ratio, engine supercharging,

hydrogen or gasoline blends, etc.) have been and are still being tested. The first detailed research document using ammonia in SI engines was performed in the 1960s in a one single cylinder Collaborative Research Fuel (CFR) engine. The initial study [20] using pure ammonia showed poor performance with high ammonia slip and NO_x in the exhaust gases. The maximum indicated thermal efficiency observed was 21%, very low in comparison to gasoline performance (38%). The performance and emissions were greatly improved (close to gasoline) by implementing supercharging, or adding hydrogen to the mixtures (optimal around 2% by mass) or increasing the Compression Ratio (CR). In [21] it was documented that by running at 1800 rpm with a CR of 8, 4-5% (by mass) of hydrogen was required whatever the Equivalence Ratio (ER). However, and as expected, high specific fuel consumption (more than twice that of gasoline) and a bad indicated outputs (70% lower than for gasoline) were found. Last, in [23] it was concluded that NO_x emissions were much higher than for conventional fossil gasoline fuels. After this period of interest towards ammonia for SI engines, very little progress was made over 40 years. It is only in the late 2000s that it regained interest. Therefore, within the last 15 years, SI CFR as well as commercial single or multi-cylinders engines have been tested with a variety of fuel blends such as ammonia/gasoline, ammonia/methane, ammonia/alcohol and ammonia/hydrogen. An overview of all published research studies (to the knowledge of the authors) is provided in Table 2 and informs about different trends in their approach.

Table 2. Main studies and literature results on the use of ammonia in SI engines.
(CD = Cylinder Displacement, H₂* = H₂ introduced by means of on-board ammonia reformer)

Authors	Type of engine	CD (l)	CR	Engine speed (rpm)	NH ₃ (%vol.)	Fuel promoter
Cornelius et al., 1966 [17]	CFR	0.44	9.4 to 18	800 to 4000	85 to 100	H ₂
Starkman et al., 1967 [18]	CFR	0.625	6 to 10	1000 to 1800	25 to 100	H ₂ *
Sawyer et al., 1968 [19]	CFR	0.625	7 and 10	1800	25 to 100	H ₂ *
Grannell et al., 2008 [12]	CFR	0.625	8 to 16	1000 to 1600	0 to 70	Gasoline
Grannell et al., 2009 [20]			10	1000 to 1600	0 to 100	
Susumu et al., 2010 [9]	Toyota	0.633	6.1	3600	50	H ₂ *
Mørch et al., 2011 [21]	CFR	0.612	6.23 to 13.58	1200	5 to 100	H ₂

Koike et al., 2012 [22]	Toyota Single-cyl- inder	0.5	14	1200	40 to 90	H ₂
					0 to 60	Gasoline
				800	100	H ₂ *
Westlye et al., 2013 [23]	CFR	0.612	7 to 15	1000	80	H ₂
Frigo and Gen- toli, 2012 [24] Comotti and Frigo, 2015 [25]	Lombar- dini 2 cylinders	0.505	10.7	1100 2500 to 5000	As high as possible	H ₂ *
Ryu et al., 2014 [26]	CFR	0.611	10	1800	0 to 80	Gasoline
Ryu et al., 2014 [26]					As high as possible	Gasoline + H ₂ *
Woo et al., 2014 [27]	Hyundai 3 cylinders	0.998	10.5	1400	0 to 80	Gasoline
Haputhanthri et al., 2015 [28]	In-line 4 cylinders	2.384	10.4	1900 to 5000	up to 18%	Gasoline + ethanol (0 to 30%)
Lhuillier et al., 2019 [29]	PSA 1 cylinder /4 fueled	0.4	10.5	1500	85 to 100	H ₂
Lhuillier et al., 2019 [30]					85 to 95	H ₂
Lhuillier et al., 2020 [31]					40 to 100	H ₂
Lhuillier et al., 2021 [32]					85 to 100	H ₂
					85 to 95	CH ₄
Mounaïm-Rous- selle et al., 2021 [34]				650, 1000, 2000	80 to 100	H ₂
Koike et al. 2019 [35]	Single cyl- inder	0.5	13.8	1200	60 (%en- ergy frac- tion)	H ₂
Koike et al., 2021 [36]	Toyota 4 cyl.	0.9	9	Cold start (from 0 to 1000 rpm)	100	H ₂ *
Valera-Medina and Banares-Al- cantara 2020 [37]	Q3.3 TSI Engine	3.3	11.6	1500 rpm	70	H ₂ and CH ₄

Oh et al., 2021 [38]	Heavy duty 6 cyl.	1.8	10.5	850 rpm	0 to 50	Natural gas
Salek et al. 2021 [39]	Kia 4 cyl.	0.5	10.5	1000 to 7000	0 to 15	gasoline/ethanol

2.1 Gasoline/Ammonia blend

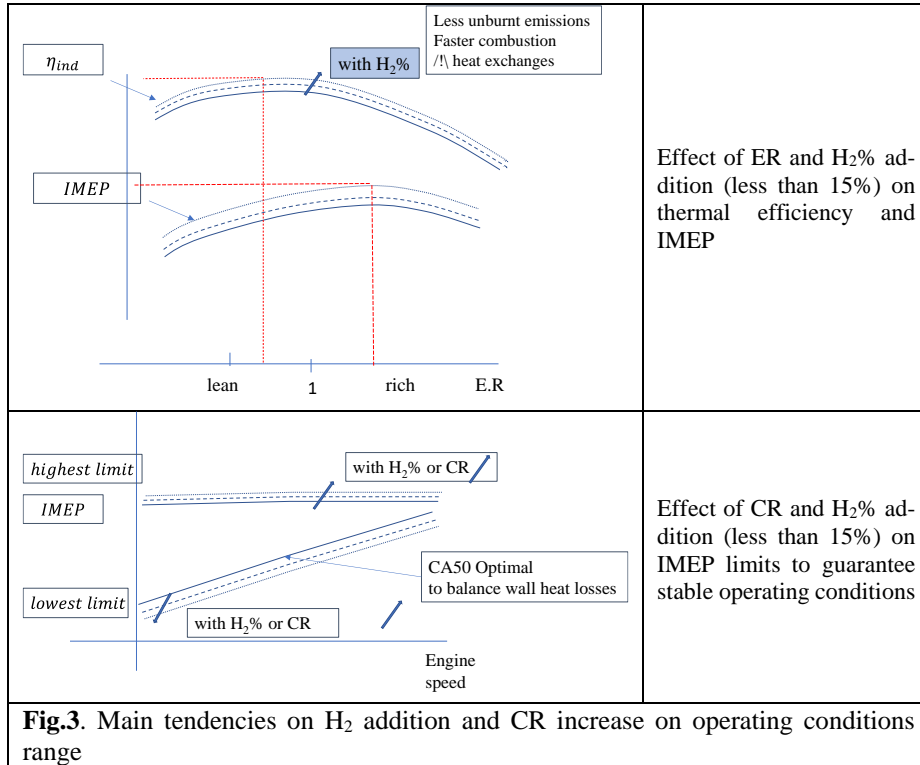
All studies of gasoline/ammonia mixtures revealed that the spark timing must be advanced to reach satisfying combustion [20, 26, 22, 27]. While testing a Hyundai 3 cylinder engine, Woo et al. [27] observed a heat release rate about 25% lower for a blend 30%NH₃/70%Gasoline than for pure gasoline. Grannell et al. [12, 20] obtained good results for a blend 70%NH₃/30% gasoline, and recommended to improve the performance by using supercharging to take advantage of the advanced spark timing. An increase in NO_x emissions was observed. These emissions seemed proportional to the amount of ammonia in the fuel blend. Haputhanthri et al. [29] stated that using gasoline blend with 12.9% ammonia and 20% ethanol (to increase the solubility of ammonia) allowed the blend to keep the same performance while reducing HC and NO_x emissions. Ryu et al.[26] suggested that the overall brake specific energy consumption was similar for gasoline alone with some ammonia/gasoline mixtures tested. They also found that the unit performance was significantly increased when a catalytic reformer was adopted to help ammonia dissociation into hydrogen.

2.2 Methane/ammonia blend

Very few recent studies [33, 37] have looked at the potential of mixing ammonia with natural gas as a combustion promoter but also as another way to contribute to decarbonizing if the gas comes from biomass or waste. The experiment performed by Lhuillier et al. [32] on methane/ammonia blend showed that the energy released was much lower than expected. Especially, when the fraction of CH₄ was increased, the authors observed a delay and lower and broader heat release rate. In [36], low engine speed and low load were selected to evaluate the potential of ammonia/natural gas blends for possible marine applications. They substituted without important issue 50% of natural gas, inducing a decrease of CO₂ emissions of up to 28%. As in most studies with ammonia, the cycle to cycle combustion is not sufficiently stable below an ER of 0.7, with some misfired cycles. Further tests performed by Valera-Medina et al [37] showed that the transition from ammonia/methane conditions due to ammonia/hydrogen had a clear, expected decline in CO₂ emissions. Interestingly, high NO_x was considerably dropped in the absence of methane, a phenomenon related to the high deNO_xing potential of ammonia and the NH path to recombine with OH instead of carbon-based radicals that promote the emissions path NH→HNO→NO. Its narrow flammable limits range itself.

2.3 Ammonia helped or not by hydrogen

When hydrogen is chosen as a fuel promoter, it can be introduced either via pressurized tanks connected to flowmeter devices for both simplicity and control of the setup, or by means of a reformer or ‘cracker’ (catalytic or thermal as recently described in [36]) to induce ammonia dissociation to H_2 . Comotti and Frigo [25] proposed that the later solution could exploit the heat of the exhaust gas to perform the dissociation, and it is therefore appropriate for compact transport application as no hydrogen tank would be needed. Mørch et al. [21] also suggested that exhaust heat could be used not only for catalytic dissociation but also to desorb ammonia stored in metal ammine complexes and then being used as a fuel upstream the combustion chamber. As first identified in the 1960s, the latest studies confirmed that a stable combustion in SI engine requires hydrogen in the blend. The minimum value is not universal until now as a function of the various criteria: 5% of H_2 by volume to avoid misfire [21, 30] or 10% H_2 by volume reaching similar energy output levels comparable to conventional gasoline [24, 25, 30, 31]. At slightly boosted conditions with 10% v/v H_2 or less, Lhuillier et al. [29] attained indicated efficiencies >37% for lean mixture close to stoichiometry. It was observed that the higher the load, the lower the hydrogen required for stable combustion [24, 25]. Moreover, satisfying adequate combustion behavior, stability was even achieved for 100% ammonia under very high loads [22, 33]. The highest efficiencies usually occur for equivalence ratios (ER) just above one but decrease with H_2 content increase. Furthermore, these studies clearly conclude that a higher CR will provide a better indicated efficiency [21,30] or as some have suggested [9] would enable the design optimized ignition devices for ammonia-fuel engines. Several studies have been focused on the cold start issues [24, 33, 35] related to the difficulties of reaching low load. Koike et al. [36] explored the promising possibility of a reformer to favor the cold start of the engine before reaching sufficient heating of the system to guarantee stable operation with only fueled with ammonia. As summarized in [35], catalytic pyrolyzer or autothermal reformer can be used to boost ammonia combustion with H_2 . The main difference is due to the temperature required for the process, even if the autothermal reformer does not require additional heat, to start the process, the addition of an electric heater is needed to activate the catalyst only in the initial combustion stage. Recently, Mounaïm-Rousselle et al. [12] provided, for the first time, data about the potential of a retrofitted compression ignition engine, where a spark plug was set instead of the diesel injector. Although the in-cylinder flow-fields are not optimal for premixed combustion, due to the swirl motion instead of a tumble one, increasing the compression ratio (up to 17) clearly showed the improvement in the stabilization of the operation of ammonia-only engines, especially at very low load and low speed. Similarly, Valera-Medina et al. [37] demonstrated that engines designed for natural gas could employ ammonia/hydrogen blends for powers ~20kW whilst ensuring proper combustion features. It was recognized that further improvements to the injection/ignition systems were required for optimized operation are promising and the main tendencies are highlighted in Figures 3.



3 Ammonia CI engine

In the case of the Compression Ignition engine, due to the auto-ignition resistance of ammonia, it requires a very high Compression Ratio, at least 35:1 as argued in [39, 40]. Therefore, as summarized in [17], only a few studies can be found in world literature between the 1970s and 2010s. As for SI engine, ammonia combustion in CI engines can be promoted by mixing with other fuels to use more usual CR engines, but also with only a small quantity of reactive fuel [42-43]. Garabedian and Johnson [40] concluded that conversion of CI Engines to spark ignition mode can be a good solution to lift the various barriers as ammonia has several issues related to combustion in CI mode. Recent studies [12] improved this concept but also opened some new pathways about the use of Diesel engine with ammonia, which needs to be ignited by a spark. Table 3 gives an overview of all research studies (to the knowledge of the authors).

Table 3. Main studies and literature results on the use of ammonia in CI engines.
(CD = Cylinder Displacement)

Authors	Type of engine	Cylinder volume (l)	CR	Engine regime (rpm)	NH ₃ amount (%vol.)	Fuel promoter
Gray et al. 1960 [42]	CFR	0.625	35 to 26	1000 to 1800	Up to maximum	Diesel (DI) ignition promoter (H ₂ , hydrazine..)
Pearsall and Garabidian, 1967 [44]	CFR	0.625	20 to 25	1000 to 1800	Up to maximum	H ₂ , acetylene, butane,
Starkman et al., 1968 [37]	CFR	0.625	16 to 24	1000 to 1800	25 to 100	SACI
Bro and Petersen, 1977 [45]	CFR	0.625	8 to 16	1000 to 1600	0 to 70	Diesel (DI)
Ryu et al., 2014 [48]		0.32	20	3600	0 to 60	DME (pre-mixed)
Reiter et Kong, 2011 [45]	JohnDeere 4 cyl.	1.125	17	1000	0 to 95 (power%)	Diesel (DI)
Niki et al. 2016 [48]				1500	100%	Diesel pilot
Sahim et al., 2018 [49]	Palmera Single cylinder	0.21	20	2000 to 3000	2 to 10 (25%NH ₃ +75%H ₂ O)	Diesel (DI)
Tai et al., 2017 [47]	MAN 4 cylinders	0.625	18.5	2400	90 (Energy fraction)	Diesel, Diesel/Kerosene (DI)
Mounaïm-Rousselle et al. 2021 [12]	PSA Single cylinder engine	0.4	14 to 17	650, 1000, 2000	100	Diesel engine Spark ignited
Pochet et al. 2020 [54, 55]	Single cylinder engine	0.5	16:1	1500	61	HCCI H ₂

Pochet et al. 2019 [53]	Yanmar- Single cyl- inder en- gine	0.435	23:1	1500	94	HCCI H ₂
----------------------------	---	-------	------	------	----	------------------------

3.1 100% Ammonia

Gray et al. [44] achieved combustion of ammonia for compression ratios of 35:1 with an intake air temperature above 423K. They also found that high-temperature glow coils improved the ammonia ignition. In [40], a first experiment with liquid ammonia direct injection was performed. However, some issues were raised due to the ammonia vaporization effect before it reached the injection nozzles. The authors used a heat exchanger to cool the liquid ammonia before the injection pump. Unfortunately, even after solving this problem, no combustion was observed. Another attempt was conducted using port injection of gaseous ammonia along with direct injection of liquid ammonia. Ammonia combustion occurred at 1200 rpm, but was not self-sustainable beyond this value.

3.2 Ammonia helped by Diesel pilot injection

Gray et al. [44] also performed experiments by considering diesel as the ignition source for ammonia in a dual-fuel engine. They were able to operate the engine with a compression ratio of 15.2:1 compared to 35:1 using only ammonia as a fuel. It was also found that proper combustion was observed when ammonia was injected in the cylinder no later than 40 CAD (Crank Angle Degree) before the end of the diesel injection. Late injection of ammonia led to misfire. In [40] the influence of diesel cetane number was studied and the results concluded that a diesel with a 50 cetane number provided optimum performance with the highest power and the shortest ignition delay. The effect of diesel quantity supplied to the engine was also evaluated. In [45] the investigation was conducted at different loads and engine regimes with an ammonia energy share ratio up to 95%. The results showed that combustion efficiency of around 95% was attained for ammonia rates between 40-80% with a reduction of NO_x emissions of up to 60% as compared to pure diesel operation. Niki et al [46] studied the influence of gaseous ammonia mixing in intake charges of a CI engine. It was found that enhancing the ammonia supply and keeping the output power constant result in lower compression and peak pressure with an increase in ignition delay leading to the increase of ammonia slip.

3.3 Ammonia and other fuels

From the first studies that considered ammonia as a fuel for CI engine, different researches [44, 48] considered different kinds of fuel doping agents to enhance the ignition, such as hydrogen, amyl-nitrate, dimethyl hydrazine, acetylene, and others. It was observed that ammonia combustion is highly dependent on the pilot ignition source. In [48], the results showed that acetylene delivers the best performance for normal compression ratio operation but for higher compression ratio, hydrogen provides

better performance. Tay et al. [49] studied an ammonia fueled CI engine with diesel/kerosene or kerosene as a pilot fuel. The authors observed that the ignition was earlier compared to diesel pilot fuel, with a better, more complete combustion of ammonia. Other studies were focused on the use of ammonia-DME mixtures in CI engines [50]. It was found that performance of the engine deteriorated when ammonia share was augmented, and beyond an ammonia share of 60%, the results denoted acute cycle to cycle variations. The authors recommended that by using higher injection pressure, the mixing of fuel-air should be increased, which results in better combustion. A recent study [51] focused on the potential of adding some ammonia solutions in Diesel CI engines to mitigate carbon emission issues, but even if the performance was enhanced by the ammonia solution introduction, the carbon emissions were not improved.

4 Ammonia for HCCI engines

Amongst the potential engine technologies available to use ammonia as a fuel for energy or transportation, the Homogeneous Charge Compression Ignition (HCCI) engine presents several assets. This particular engine enables a very low fuel consumption since it operates with very lean mixtures and with a high efficiency. Its major drawback lies in the difficulty of controlling the combustion phasing since the ignition of the air/fuel load is mainly driven by the chemistry, thus making HCCI unsuitable for transportation. However, it could be very interesting for stationary applications such as combined heat and power (CHP) plants where high efficiency is reachable.

However, running a HCCI engine with a high efficiency is usually limited in the search of a compromise with clean operation. As in the CI engine, a high compression ratio as well as high intake pressure and temperature conditions are required. Unfortunately, the low power output of the HCCI engine, combined with the low Lower Heating Value (LHV) of ammonia and the high intake temperature required reduce the power density of such an application. Moreover, the HCCI engine is well known for its low temperature combustion (LTC) mode obtained through very lean fuel/air mixtures. This fact leads to very low NO_x and soot levels; this remains challenging with ammonia as a fuel due to its nitrogen content.

During the past years, only a few studies covered the use of ammonia in HCCI engine. Van Blarigan [51] indeed proved the possibility of using only ammonia as a fuel in HCCI mode without preheating but with a compression ratio of 40-60:1, very far from the current commercially available engines. More recently, in [54-56], different aspects of ammonia as a HCCI fuel were investigated, for example, mixing and intake conditions requirements, fundamental combustion properties, ignition delay of ammonia and ammonia/hydrogen blend in LTC conditions, CR improvements between 16:1 to 23:1 by using two different engines, etc. It was found that increasing the compression ratio helps to decrease the intake temperature requirement, which remains still too high in terms of heating power requirement and leads to a mixture density decrease and therefore less power output. Finally, with such intake temperature, the temperature at the Top Dead Center might be so high that LTC conditions will be no longer met, leading to thermal NO_x formation and thus a counteract of the benefits of the HCCI engine itself. Regarding the pressure intake condition, increasing it can surely help the process:

a 2 bar intake pressure (vs. 1 bar) allows to decrease the required intake temperature by 60K. Therefore, the difficulty of using neat ammonia as a fuel in a HCCI engine with conventional compression ratios is highlighted. With 10% of H₂ in the fuel blend at equivalence ratios ~0.4, an intake pressure of 2 bar and a CR=20:1, the condition results in a 100K decrease of the intake temperature from 540 to 440 K. With 50% of H₂, the required intake temperature even goes down to 400K under similar conditions. As an example, with the lowest CR and having the limits of 1.5 bar and 483 K at the intake, it was not possible to run the engine with more than 61% of NH₃ with NH₃/H₂ fuel blends (with an 0.27 ER). The addition of ammonia in H₂/NH₃ blends induced a decrease of Heat Release Rate due to the decrease of OH, as more intermediate species that are consuming OH are produced. Moreover, hydrogen and ammonia share their combustion radicals resulting in a damped combustion because there are simply more steps for the combustion when adding ammonia compared to pure hydrogen (consequence of the nitrogen-based radicals). To promote auto-ignition of ammonia, ozone seeding was also tested as an oxidizing species to shorten the ignition delay. However, no effect on the auto-ignition promotion was founded from 0 to 140 ppm of ozone.

In other engines (highest CR), researchers were able to burn ammonia/hydrogen blended with ammonia content varying from 0 to 94% in the mixture. Due to the damping effect of ammonia on the combustion, adding ammonia to the fuel blend allows a higher equivalence ratio and therefore leads to a higher energy output. The obtained indicated efficiency as a function of the ammonia content was constant for the maximal energy output ~37%. Finally, the studies concluded that to use a Diesel engine retrofitted to HCCI for ammonia requires many optimizations in the design in terms of compression ratio, crevices, stroke-to-bore ratio as well as intake conditions (turbocharged) to efficiently operate with high ammonia content.

5 Emissions trends for ammonia engine.

5.1 General considerations

When ammonia is combusted mainly nitric oxide (NO) is formed, with small traces of nitrogen dioxide (NO₂) and nitrous oxide (N₂O). These molecules are precursors of acid rain, photochemical smog and greenhouse effects, especially N₂O. Although NO is not hazardous at ambient level, it oxidises into NO₂ in the atmosphere relatively quickly and is a major pollutant of concern in many cities. NO₂ can cause allergic reactions and lung dysfunctionality until it is fatal. N₂O is also an unwanted emission as its Global Warming Potential is 300 times that of CO₂. Interestingly, environmentalists have been also studying the effect of NO_x and unburned ammonia (which is another detrimental pollutant obtained from engines running on the fuel as a consequence of inefficient combustion) on the production of fine particle matter (diameters less than 2.5 μm). The main concern of these particles is that they can pass through skin or alveoli, thus reaching the bloodstream. Ammonium nitrate (NH₄NO₃) and ammonium sulphate ((NH₄)₂SO₄) are formed in the presence of ammonia, sulphates and nitrogen oxides, thus leading to particle matter. Nitrogen oxide (NO_x) emissions are inherently one of the main challenges to solve in the development of ammonia powered technologies.

There are three main mechanisms for the formation of NO_x in combustion systems. These mechanisms are,

- Thermal NO (Zeldovich) mechanism: the most important source of nitrogen oxides at high temperature combustion.
- Prompt NO: initiated by combination of CH_n-radicals on the nitrogen molecule, leading to cyanide-nitrogen NCN formation as a precursor of the formation of nitrogen oxides.
- Fuel NO_x formation: caused by the nitrogen atom fixed into the fuel itself.

First kinetics mechanism of ammonia oxidation [56] demonstrated that NO/N₂ formation mainly depended on the path of NH_x radicals, but in [57] the description of the important reactions for NO formation highlighted the importance of thermal NO_x for high temperature combustion using hydrogenated blends, whilst OH plays a more crucial role with pure ammonia. From that study, different improvements of these mechanisms have been and are still done. Further analyses carried out in [58] indicated that HNO from NH₂+O reactions was the main precursor of NO formation. Moreover, when other fuels are used simultaneously with ammonia to enhance its ignition, there are some interactions between other fuels and NH₃ chemistry for NO_x formation. It is clear that although researchers are getting closer to fully understanding the kinetics of NO_x formation in ammonia flames, there are many complexities that need to be addressed before a “universal” model is available for the combustion of such a chemical. In [59] a vast amount of literature on the subject of modelling nitrogen chemistry in combustion is compiled with some analyses about previous and current models. Further, fuel NO formation/reduction appears to be dependent on the O/H radical pool, which varies depending on equivalence ratio, pressure conditions and other fuel presences.

The NO₂ formation reaction is shown by equation (3) but in the post-flame region, NO₂ is converted back to NO, through the reaction in equation (4).



In SI engine, as the fuel and air are premixed, the combustion chamber temperature is nearly uniform after the flame propagation in such systems, which results in a NO₂/NO_x ratio less than 2 %. On the other hand, in CI engines, as the combustion is mixing controlled, with a wide distribution of cool regions, a higher ratio of NO₂/NO_x is expected. N₂O forms when NH₃ is in the presence of NO and NO₂ at low temperature. This formation mechanism is one part of the Selective Non-Catalytic Reduction mechanism.

5.2 Exhaust emissions in ammonia ICE engines

The global trend observed is that more NO_x is produced for lean combustion whereas more ammonia slip has to occur for rich mixtures due to the fuel excess itself. Because of this opposite behavior, it will be necessary to apply aftertreatment devices or novel injection strategies, even for optimized fuel blends, to ensure that emissions are below limits. In [24], the comparison between convention fossil fuels indicated that even if NO peaks are reached under lean mixtures in the case of ammonia combustion, these peaks tend to occur at leaner operating condition when using ammonia/hydrogen blends (ie. 35% excess air for ammonia/hydrogen blend instead of 10% for HC). From all previous studies in SI engines, it has also been concluded that the substitution of one part of NH₃ by H₂ does not lead to a decrease of NO_x emissions due to the decrease of nitrogenated fuel itself, but instead leads to an increase of NO_x with the increase of hydrogen content. All studies concluded that NO is the major contributor to total NO_x in these systems. Last, N₂O emissions were always found at very low quantities in these studies (less than 100 ppm), which confirms the low impact of NH₃ combustion in global warming. However, it must be emphasized that N₂O needs to be carefully addressed during the combustion even if as underlined in [33], it corresponds to an equivalent quantity of ammonia blends at certain equivalence ratios, at 1.5% CO₂ in emissions.

Ammonia slip is due to the crevices of the combustion chamber, out of which the piston top land crevice has the greatest contribution [12, 24, 55]. The engine architecture (piston design, crevice, compression ratio, squish zone for diesel design engine, etc.) plays an important role in the release of this ammonia slip. Therefore, it is difficult to predict from any simulation tools the ammonia amount at the exhaust as it should occur only when ammonia is in excess. This mechanism depends on the combustion characteristics of the fuel, which is governed by the heat loss to the combustion chamber walls. Such mechanism describes that the fuel that escapes the combustion in crevices is proportional to the in-cylinder pressure. When gaseous ammonia is used as a fuel, the formation of unburned ammonia is closer to liquid ammonia as underlined in [24]. Figure 4 summarizes the key behaviors from the different studies approaching these phenomena. Most of previous studies based on exhaust emission measurements have been done with Fourier Transformation InfraRed Spectroscopy without considering H₂ emissions. More recent studies [12, 32-34] performed the measurement of this molecule using thermal conductivity sensors, and they concluded that even if H₂ is not yet a regulated pollutant species, its release to the atmosphere is undesirable. Researchers indicated that a level of H₂ at the exhaust about 1.5%-2% should be set as a maximum, a condition that should be followed not only when H₂ is added to ammonia at the intake. For example, by increasing the compression ratio, the cracking of ammonia to hydrogen inside the combustion chamber could be induced near the TDC as illustrated in Figure 5, where estimated concentrations of NH₃, H₂ and average in-cylinder temperature from 2 zones-0D SI engine simulations (Chemkin PRO) have been displayed for conditions presented in [12]. These works need some more dedicated studies in the

future, especially targeting engine technology that can employ ammonia decomposition inside the cylinder and that lead to this H₂ emission.

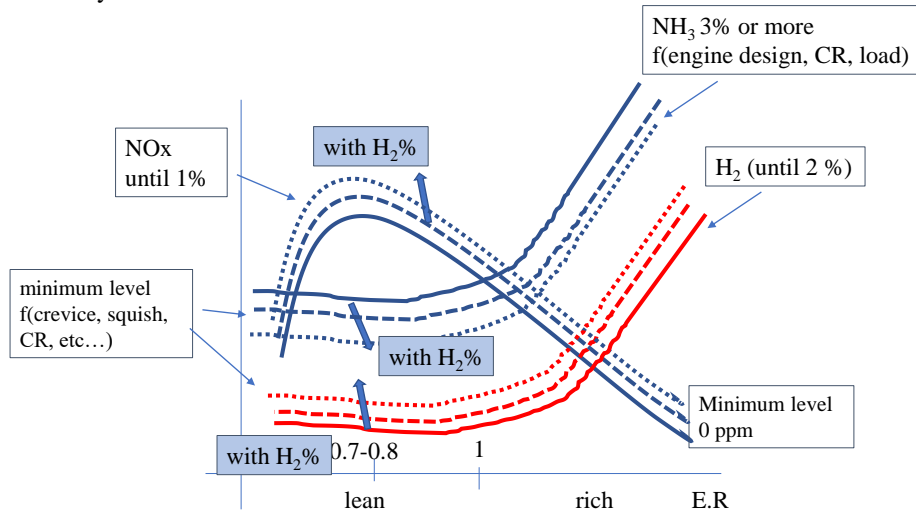


Fig. 4. Exhaust emissions tendency as a function of ER and % of H₂ in blend.

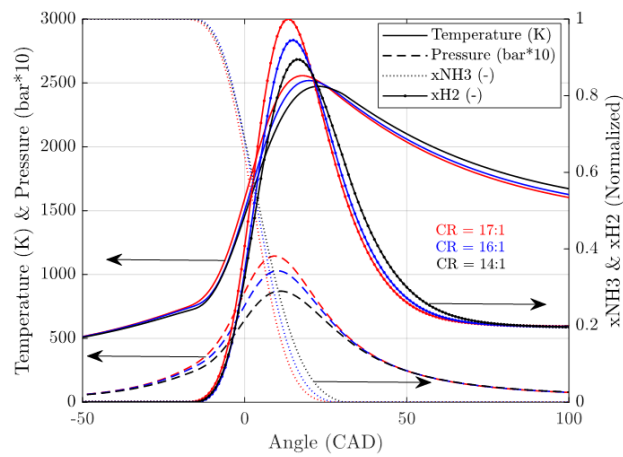


Fig. 5. Example of the effects of Compression Ratio on ammonia oxidation and cracking (2 zones SI engine simulation with Chemkin PRO using Stagni et al. [57] kinetic mechanism [

5.3 NO_x/NH₃ trade-off solution for ammonia ICE engines

To decrease ammonia slip and NO_x, different strategies are already considered. Recently, in [34], the potential of intake gases dilution has been tested: a maximum of 8% of dilution can still provide stable operating conditions and can allow 40% decrease of NO_x without any NH₃ emissions effect. Another classical mean is to optimise injection

strategies in the case of dual-fuel engines as in [62, 63], where advancing and splitting the diesel injection leads to an increase of the combustion temperature which prevents N_2O formation as well as enhancing the combustion rate of ammonia.

A final point relates to the implementation of selective catalytic reduction (SCR) systems to mitigate NO_x/NH_3 as far as possible. Even if the first tests related in [22] proved that it could be efficient and to reduce emissions to the same level than gasoline, as a function of the emissions-reduction strategy and engine operating conditions, the design of appropriate SCR will be certainly required. It is also interesting to note that in [35], by using on-board cracker to warm the engine, nearly zero NH_3 emissions were achieved during cold start and fast idle by adsorbing unburned NH_3 only through a three-way catalyst.

6 Conclusion and future

Figure 5 summarizes all potential solutions to implement ammonia in IC engines. The combustion of ammonia as a fuel in ICE remains very challenging even if the engine design is more and more adapted. However, the use of the molecule will contribute to reaching zero-carbon emission targets. For any engine combustion modes, i.e. SI, CI or HCCI to overcome the previously addressed ignition difficulties, the seeding of ammonia/air mixture by an amount of H_2 is required to extend the stable operating conditions range as far as possible. From most recent studies, the improvement of ammonia engines during cold starts still needs to be addressed. As done in [26, 36, 56], the use of an on-board cracker should be a good solution, particularly for cold start issues. The recent studies are increasingly confident in this device, especially in a recent study [36] where the potential control of ammonia combustion at the engine through a thermal reformer is clearly demonstrated.

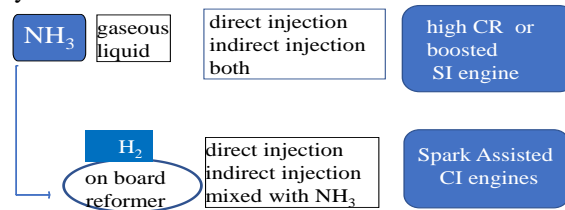


Fig. 4. Different technical issues for fully ammonia ICE (Figure 5?)

Additional technical barriers still need to be removed. First, more consistent studies are required to optimize the ammonia supply to the engine. In most of the studies, the simplest method to inject ammonia is using its gaseous form at the injection port. However, some adverse effects can be induced due to the volume efficiency reduction because of the air displacement caused by ammonia. Direct injection of gaseous ammonia could be an advantageous solution for maintaining global efficiency, but perhaps also it can contribute to decrease ammonia slip and increase the output power. Only one study has focus on the injection and mixing characteristics of gaseous ammonia jets [65]. Simultaneously, due to its low energy content, liquid direct injection could also be advantageous, especially to retrofit diesel engines. However, vaporization heat is so

important that the decrease of in-cylinder temperature could be harmful to the combustion itself. Moreover, due to the specificity of its saturating vapour curve, the process can induce fast ammonia atomisation during the injection process itself, as recently studied in [64]. Finally, the ammonia solubility in lubrication oil was not known until now, and the contribution of ammonia slip from ammonia absorption and desorption in oil layers has to be evaluated.

In view of the increasing number of announcements concerning the maritime sector in particular, a lot of work is being done in order to predict the behavior of ammonia-fueled engines, by using experiments or modelling tools as in [66-69]. Whilst the knowledge about ammonia oxidation is still increasing, ammonia combustion in IC engines still remains far from complete as underlined in [11, 12, 33] and requires new studies to provide accurate data whilst improving the prediction of simulation tools to design and optimize future ammonia engines.

References

1. Valera-Medina, A.; Amer-Hatem, F.; Azad, A. K.; Dedoussi, I. C. ; de Joannon, M.; Fernandes, R. X.; Glarborg, P.; Hashemi, H.; He, X. ; Mashruk, S.; McGowan, J. ; Mounaim-Rousselle, C. ; Ortiz-Prado, A. ; Ortiz-Valera, A. ; Rossetti, I. ; Shu, B. ; Yehia, M. ; Xiao, H. ; Costa, M. *Energy & Fuels* **2021** 35 (9), 6964-7029.
2. Angeles, D.A., Tan, R.R., Aviso, K.B., Are, K.R.A.G., Razon, L.F., 2018. Fuzzy optimization of the automotive ammonia fuel cycle. *J. Clean. Prod.* 186, 877–882.
3. Bicer, Y., Dincer, I., 2018. Life cycle assessment of ammonia utilization in city transportation and power generation. *J. Clean. Prod.* 170, 1594–1601.
4. Zhou, M.; Wang, Y; Chu, Y; Tang, Y; Tian, K; Zheng, S. ; Chen, J.; Wang, Z.; Ammonia as an environmentally benign energy carrier for the fast growth of China, *Energy Procedia*, Volume 158, 2019, pp. 4986-4991.
5. Sousa Cardoso, J., Silva, V., Rocha, R.C., Hall, M.C., Costa, M., Eusébio, D., Ammonia as an energy vector: Current and future prospects for low-carbon fuel applications in internal combustion engines, *Journal of Cleaner Production*, Volume 296, 2021
6. Koch, E., Ammonia as a fuel for motor buses. *J. Inst. Pet.* 31, 21–32, 1949.
7. Hodgson, J. W. Alternate fuels for transportation. Part III. Ammonia for the automobile. *Mech. Eng.; Journal Volume: 96:7, 1974-07-01*
8. Valera-Medina A., Xiao, H., Owen-Jones, M., David, W.I.F., Bowen, P.J., Ammonia for power, *Progress in Energy and Combustion Science*, Volume 69, 2018, Pages 63-102
9. <https://nh3fuel.com/index.php/news/13-multimedia/20-2007-10-16-ammonia-conference-presentation>, last accessed 2021/07/30
10. Susumu, K., Nakamura, N., Shimizu, R., Sugimoto, T., Kim, K.-O., 2009. Ammonia burning internal combustion engine. International Patent No WO 2010/079846 A1
11. Mounaïm-Rousselle C., Brequigny P. (2020) Ammonia as Fuel for Low-Carbon Spark-Ignition Engines of Tomorrow's Passenger Cars. *Front. Mech. Eng.* 6:70, 2020
12. Mounaïm-Rousselle C., Mercier A., Brequigny P., Dumand C., Bouriot J., Houillé S., Performance of Ammonia fuel in the case of Spark Assisted Compression Ignition engine, Special issue on the current and future use of H₂ and H₂ based e-fuels in combustion engines and fuel cells, *International Journal of Engine Research*, to appear, 2021

13. Grannell, S.M., Assanis, D.N., Bohac, S.V., Gillespie, D.E.: The Fuel Mix Limits and Efficiency of a Stoichiometric, Ammonia, and Gasoline Dual Fueled Spark Ignition Engine. *Journal of Engineering for Gas Turbines and Power*. 130, 042802 (2008).
14. Szybist, J.P., Busch, S., McCormick, R.L., Pihl, J.A., Splitter, D.A., Ratcliff, M.A., Kolodziej, C.P., Storey, J.M.E., Moses-DeBusk, M., Vuilleumier, D., Sjöberg, M., Sluder, C.S., Rockstroh, T., Miles, P.: What fuel properties enable higher thermal efficiency in spark-ignited engines? *Progress in Energy and Combustion Science*. 82, 100876 (2021).
15. Fioroni, G.M., Fouts, L., Christensen, E., Anderson, J.E., McCormick, R.L.: Measurement of Heat of Vaporization for Research Gasolines and Ethanol Blends by DSC/TGA. *Energy Fuels*. 32, 12607–12616 (2018).
16. Ryu, K., Zacharakis-Jutz, G.E., Kong, S.-C.: Performance enhancement of ammonia-fueled engine by using dissociation catalyst for hydrogen generation. *International Journal of Hydrogen Energy*. 39, 2390–2398 (2014).
17. Dimitriou P., Jawad R., A review of ammonia as a compression ignition engine fuel, *International Journal of Hydrogen Energy*, Volume 45, Issue 11, 2020, Pages 7098-7118,
18. Cornelius, W., Huellmantel, L., and Mitchell, H., Ammonia as an Engine Fuel. Presented at the 1965 International Automotive Engineering Congress and Exposition, SAE Technical Paper 650052, 1965
19. Starkman, E.S., Newhall, H.K., Sutton, R., Maguire, T., Farbar, L., Ammonia as a Spark Ignition Engine Fuel: Theory and Application. Presented at the 1966 Automotive Engineering Congress and Exposition, SAE Technical Paper 660155, 1966.
20. Sawyer, R., Starkman, E., Muzio, L., Schmidt, W.: Oxides of Nitrogen in the Combustion Products of an Ammonia Fueled Reciprocating Engine. Presented at the Mid-Year International Automotive Engineering Meeting (1968), SAE Technical Paper 680401, 1968.
21. Grannell, S.M., Assanis, D.N., Gillespie, D.E., Bohac, S.V.: Exhaust Emissions From a Stoichiometric, Ammonia and Gasoline Dual Fueled Spark Ignition Engine. In: ASME 2009 Internal Combustion Engine Division Spring Technical Conference. pp. 135–141. ASMEDC, Milwaukee, Wisconsin, USA (2009).
22. Mørch, C.S., Bjerre, A., Gøttrup, M.P., Sorenson, S.C., Schramm, J.: Ammonia/hydrogen mixtures in an SI-engine: Engine performance and analysis of a proposed fuel system. *Fuel*. 90, 854–864 (2011).
23. Koike M., Miyagawa H., Suzuoki T., Ogasawara K.: Ammonia as a hydrogen energy carrier and its application to internal combustion engines. In: *Sustainable Vehicle Technologies*. pp. 61–70 (2012).
24. Westlye, F.R., Ivarsson, A., Schramm, J.: Experimental investigation of nitrogen-based emissions from an ammonia fueled SI-engine. *Fuel*. 111, 239–247 (2013)
25. Frigo, S., Gentili, R.: Analysis of the behavior of a 4-stroke Si engine fueled with ammonia and hydrogen. *International Journal of Hydrogen Energy*. 38, 1607–1615 (2012)
26. Comotti, M., Frigo, S., Hydrogen generation system for ammonia–hydrogen fueled internal combustion engines. *International Journal of Hydrogen Energy*. 40, 10673–10686 (2015)
27. Ryu, K., Zacharakis-Jutz, G.E., Kong, S.-C.: Effects of gaseous ammonia direct injection on performance characteristics of a spark-ignition engine. *Applied Energy*. 116, 206–215 (2014)
28. Woo, Y., Jang, J.Y., Lee, Y.J., Kim, J.-N.: Recent progress on the Ammonia-Gasoline and the Ammonia-Diesel dual fueled internal combustion engines in Korea. Presented at the 11th NH3 Fuel Conference (2014)
29. Haputhanthri, S.O., Maxwell, T.T., Fleming, J., Austin, C.: Ammonia and Gasoline Fuel Blends for Spark Ignited Internal Combustion Engines. *Journal of Energy Resources Technology*. 137, 062201 (2015)

30. Lhuillier, C., Brequigny, P., Contino, F., Rousselle, C.,: Combustion Characteristics of Ammonia in a Modern Spark-Ignition Engine. Presented at the 14th International Conference on Engines & Vehicles, Capri, Italy September 9, SAE Tech. Pap. 2019-24-0237 (2019)
31. Lhuillier, C., Brequigny, P., Contino, F., Rousselle, C., Performance and Emissions of an Ammonia-Fueled SI Engine with Hydrogen Enrichment. SAE Tech. Pap. 2019-24-0137 (2019)
32. Lhuillier, C., Brequigny, P., Contino, F., Mounaïm-Rousselle, C.: Experimental study on ammonia/hydrogen/air combustion in spark ignition engine conditions. *Fuel*. 269, 117448 (2020)
33. Lhuillier, C., Brequigny, P., Contino, F., Mounaïm-Rousselle, C.: Experimental investigation on ammonia combustion behavior in a spark-ignition engine by means of laminar and turbulent expanding flames. *Proceedings of the Combustion Institute*. 38, 5859–5868 (2021)
34. Mounaïm-Rousselle, C.; Bréquigny, P.; Dumand, C.; Houillé, S. Operating Limits for Ammonia Fuel Spark-Ignition Engine. *Energies* **2021**, *14*, 4141 (2021)
35. Koike, M., Suzuoki, T. In-line adsorption system for reducing cold-start ammonia emissions from engines fueled with ammonia and hydrogen, *International Journal of Hydrogen Energy*, Vol. 44, Issue 60, Pages 32271-32279 (2019)
36. Koike, M., Suzuoki, T., Takeuchi, T., Homma, T., Hariu, S., Takeuchi, T. Cold-start performance of an ammonia-fueled spark ignition engine with an on-board fuel reformer, *International Journal of Hydrogen Energy*, Vol. 46, Issue 50 (2021)
37. Valera-Medina A and Banares-Alcantara R. 2020, Techno-economic challenges of ammonia as an energy vector, Chapter 7, applications. pp. 165-171
38. Oh, S., Park, C., Kim, S., Kim, Y., Choi, Y., Kim C., Natural gas–ammonia dual-fuel combustion in spark-ignited engine with various air–fuel ratios and split ratios of ammonia under part load condition, *Fuel*, Vol. 290 (2021)
39. Salek, F.; Babaie, M.; Shakeri, A.; Hosseini, S.V.; Bodisco, T.; Zare, A. Numerical Study of Engine Performance and Emissions for Port Injection of Ammonia into a Gasoline/Ethanol Dual-Fuel Spark Ignition Engine. *Appl. Sci.* **2021**, *11*, 1441.
40. Starkman, E., James, G., and Newhall, H., "Ammonia as a Diesel Engine Fuel: Theory and Application," SAE Technical Paper 670946 (1967)
41. Pearsall, T. and Garabedian, C., Combustion of Anhydrous Ammonia in Diesel Engines," SAE Technical Paper 670947 (1967)
42. Garabedian, C., Johnson, J., The theory of operation of an ammonia burning internal combustion engine, report 634681. Michigan, USA (195)
43. Grannell, S. M., Assanis, D. N. Bohac, S. V. Gillespie, D. E. :The Fuel Mix Limits and Efficiency of a Stoichiometric, Ammonia, and Gasoline Dual Fueled Spark Ignition Engine, *Journal of Engineering for Gas Turbines and Power*, Volume 130, Issue 4, pp. 042802 (2008)
44. Kong S.C, Gross C.W., : Performance characteristics of a compression-ignition engine using direct-injection ammonia–DME mixtures, *Fuel* vol. 103, 2013, pp 1069-1079 (2012)
45. Gray, D.S, Domke, C.J., Meguerian, G.H., Mieville R.L.. Ammonia Application to Reciprocating Engines. Technical report, 5 (1967).
46. Reiter A.J, Kong S.C. Demonstration of compression-ignition engine combustion using ammonia in reducing greenhouse gas emissions. *Energy and Fuels*, 22(5):2963,2971, 9 (2008)
47. Pearsall T.J., Garabedian C.G. Combustion of Anhydrous Ammonia in Diesel Engines. SAE Transactions, pages 3213-3221, 1968.
48. Bro K., Pedersen P.S., Alternative Diesel Engine Fuels: An Experimental Investigation of Methanol, Ethanol, Methane and Ammonia in a D.I. Diesel Engine with Pilot Injection, SAE 770794 (1977)

49. Niki, Y., Yoo, D.H., Hirata, K., Sekiguchi, H.. Effects of Ammonia Gas Mixed Into Intake Air on Combustion and Emissions Characteristics in Diesel Engine, ASME International, 10 (2016).
50. Tay K.L., Yang W., Li J., Zhou D., Yu W., Zhao F., Chou S.K., Mohan B., Numerical investigation on the combustion and emissions of a kerosene-diesel fueled compression ignition engine assisted by ammonia fumigation, Applied Energy, 204:1476-1488, 10 (2017)
51. Ryu, K. Zacharakis-Jutz, G.E, Kong. S.C., Performance characteristics of compression-ignition engine using high concentration of ammonia mixed with dimethyl ether. Applied Energy, 113:488-499 (2014).
52. Şahin, Z., Akcanca, I.Z., Durgun, O., Experimental investigation of the effects of ammonia solution (NH₃OH) on engine performance and exhaust emissions of a small diesel engine, Fuel, Volume 214, Pages 330-341 (2018)
53. Van Blarigan, P., Advanced internal combustion engine research, Proceedings of the 2000 US DOE Hydrogen Program Review, San Ramon, California, p. 639–56 [4] (2000)
54. Pochet M., Truedsson, I., Foucher, F., Contino, F., Jeanmart, F. Ammonia-Hydrogen Blends in Homogeneous-Charge Compression-Ignition Engine, SAE Tech. Pap. (2017-24-0087) (2017)
55. Pochet M., Jeanmart, H., Contino, F., A 22:1 Compression Ratio Ammonia-Hydrogen HCCI Engine: Combustion, Load and Emission Performances, Front. Mech. Eng. 6 (2020) 43
56. Pochet M., Use of electrofuel blends in homogeneous-charge compression-ignition engines : an experimental focus on ammonia-hydrogen. PhD Thesis, UC Louvain, Vrije Universiteit Brussel (2020)
57. Wang, W., Herreros, J.M., Tsolakis, A., York, A.P. E. Ammonia as hydrogen carrier for transportation; investigation of the ammonia exhaust gas fuel reforming, International Journal of Hydrogen Energy, Volume 38, Issue 23, 2013, Pages 9907-9917,
58. Stagni A, Cavallotti C, Arunthanayothin S, et al. An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia. Reaction Chemistry & Engineering 5(4). Royal Society of Chemistry (RSC): 696–711. (2020)
59. Miller JA, Bowman CT. Mechanism and modeling of nitrogen chemistry in combustion. Prog Energy Combust Sci 1989;15:287–338.
60. Lindstedt RP, Lockwood FC, Selim MA. Detailed Kinetic Modelling of Chemistry and Temperature Effects on Ammonia Oxidation. Combust Sci Technol 1994;99:253–76.
61. Mendiara T, Glarborg P. Ammonia chemistry in oxy-fuel combustion of methane. Combust Flame 2009;156:1937–49
62. Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. Modeling nitrogen chemistry in combustion. Prog Energy Combust Sci 2018;67:31–68.
63. Niki Y., Nitta Y., Sekiguchi H. Hirata K., Emission and combustion characteristics of diesel engine fumigated with ammonia. In ASME 2018 Internal Combustion Engine Division Fall Technical Conference, ICEF 2018, volume 1. American Society of Mechanical Engineers, 1 (2018)
64. Niki, Y. (May 31, 2021). "Reductions in Unburned Ammonia and Nitrous Oxide Emissions From an Ammonia-Assisted Diesel Engine With Early Timing Diesel Pilot Injection." ASME. *J. Eng. Gas Turbines Power*. September 2021; 143(9): 091014. <https://doi.org/10.1115/1.4051002>
65. Pelé, R.; Mounaïm-Rousselle, C.; Bréquigny, P.; Hespel, C.; Bellettre, J. First Study on Ammonia Spray Characteristics with a Current GDI Engine Injector. *Fuels* **2021**, *2*, 253-271
66. Zhang H., Li T., Chen R., Wang N., Wei Y., Wu D., Injection characteristics and fuel-air mixing process of ammonia jets in a constant volume vessel, Fuel, Volume 304, (2021), 121408

67. Wang Du, Ji C., Wang, S., Yang, J., Wang, Z., Numerical study of the premixed ammonia-hydrogen combustion under engine-relevant conditions, *International Journal of Hydrogen Energy*, Volume 46, Issue 2, 2021, Pages 2667-2683,
68. Hansson, J.; Brynolf, S.; Fridell, E.; Lehtveer, M. The Potential Role of Ammonia as Marine Fuel—Based on Energy Systems Modeling and Multi-Criteria Decision Analysis. *Sustainability* **2020**, *12*, 3265
69. Schönborn A. Aqueous solution of ammonia as marine fuel. *Proceedings of the Institution of Mechanical Engineers, Part M: Journal of Engineering for the Maritime Environment*. 2021;235(1):142-151.