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Combustion Engines
Polish Scientific Society of Combustion Engines

Ammonia as an alternative fuel to internal combustion engines

The article presents a broad review of the current knowledge on the potential of using ammonia as a fuel for internal combustion engines. A critical physicochemical and functional properties analysis of ammonia was carried out regarding fuel for internal combustion engines. Challenges related to the problems of creating a mixture and the combustion process of ammonia in both SI and CI engines were described. It was indicated that using an admixture of small amounts of fuels to ammonia to act as combustion promoters was necessary. Attention was drawn to the problems related to the exhaust emissions that occur when using ammonia or ammonia with an admixture of other fuels to power engines. The adverse effect of ammonia combustion products and ammonia itself on the lubricating engine oil was also discussed. The need to develop dedicated lubricating oils for internal combustion engines fueled with ammonia was explained.

1. Introduction

The ever-increasing demand for energy and the relentless pursuit of reducing greenhouse gas emissions (CO_2) currently present the main problems and challenges in global economics. The increases in energy production continue to come largely from fossil fuels, contributing to the growth of CO_2 emissions. Pollution from regulated and unregulated harmful exhaust components and greenhouse gas emissions are the main problems associated with the combustion of fossil fuels in internal combustion engines (ICE). In 2021, carbon dioxide emissions from the transport sector accounted for almost 23% of greenhouse gas emissions in the European Union (EU). This makes transportation the second largest source of greenhouse gas emissions after the energy supply sector [16]. As a result, the EU has committed itself to reducing greenhouse gas emissions by 55% by the year 2030. Furthermore, the target set is to achieve zero net greenhouse gas emissions by 2050. Current EU regulations are limited solely to e-mobility. They leave no room for other technologies or technological competition to achieve the adopted climate goals. This approach marks a departure from the previous, generally accepted practice, which assumed a balance between different technologies. The potential for reducing CO_2 from the existing vehicle population was also ignored [64, 65]. Meanwhile, previous experience and progress in the electrification of transport have proven that it is not proceeding as quickly as initially assumed. In addition, users of electric vehicles have indicated many inconveniences and problems related to their operation, which discourages future potential buyers from buying [64, 65]. As a result, according to Reuters, sales of new electric cars in the European Union fell by 12% in May 2024 compared to the previous year, led by a 30% drop in Germany. As a result, it has been noticed that relying on the development of only one powertrain technology can lead to dangerous, unacceptable, irreversible consequences [58, 64]. Therefore, it is so important to find new, alternative fuels with low corresponding exhaust emissions associated with the combustion process. Many manufacturers are going back and attempting to further exploit the capabilities of piston combustion engines, but using them in combination with alternative fuels [58]. Currently, the decarbonization of the transport sector is largely based on developing technologies and implementing alternative non-fossil fuels. A distinction should be made between zero-emission technology, in which hydrogen and ammonia are used, and zero-net emission technology, in which e-fuels and synthetic fuels are used [58, 64, 65]. In recent years, interest has increased in researching ammonia as a carbon-free fuel for powering piston combustion engines [71]. The mature and developed infrastructure for the production, storage and transportation of ammonia allows for its rapid diffusion in energy systems. The use of green hydrogen and renewable energy enables the production of green ammonia, making it even more attractive to the environment. One of the prerequisites for the commercial use of ammonia in power systems, such as internal combustion engines and stationary gas turbines, is a better understanding of the ignition and combustion processes of ammonia [82]. It is estimated that replacing fossil fuels with ammonia would significantly reduce the volume of CO_2 emissions (by 8–48%), depending on the use of different ammonia application strategies) [82]. However, such a solution comes with new challenges, such as unburned ammonia and N_2O emissions, among others. The combination of optimal combustion strategies and exhaust aftertreatment systems dedicated to ammonia-fueled engines can increase engine efficiency while reducing harmful emissions. Ammonia is currently one of the most popular chemical products and has one of the largest production and sales volumes worldwide. Although ammonia has been used in the past as a fuel for internal combustion engines [76], no engine powered by self-contained ammonia is currently commercially available.

2. Properties of ammonia as a fuel for combustion engines

In Table 1, key physiochemical properties of ammonia as a fuel were compared with analogous properties of other fuels, both containing carbon and carbon free [3, 11, 14, 18].

Table 1. Comparison of the physicochemical properties of ammonia with other fuels [3, 11, 14, 18]

Fuel	Ammonia	Hydrogen gas	Hydrogen liquid	LPG	CNG	Diesel	Gasoline
Calorific value [MJ/kg]	18.8	120.1	120.1	45.7	38.1	43.5	44.5
Octane number	110	> 130	> 130	112	107	N/A	90–98
Autoignition temp. [°C]	651	571	571	470	450	230	300
Flammability limit in air [vol. %]	16.25	4–75	4–75	1.81–8.86	5.0–15.0	0.6–5.5	1.4–7.6
Maximum laminar flame speed [m/s]	0.007–0.15	3.51	3.51	0.83	8.45	0.87	0.58
Energy density [MJ/m^3]	11333	2101	8539	86487	7132	36403	31074
Stoichiometric air/fuel ratio	6	34.3	–	–	17.1	14.6	14.7
Minimum ignition energy [MJ]	8.0	0.02	–	0.25	0.28	–	0.14
Quench distance [mm]	7	0.64	–	–	–	3	

Although hydrogen is now seen as the emission-free fuel of the future, it is difficult and more expensive to store than ammonia. This is due, among other things, to the high compression pressure (350–700 bar) required to make it competitive in terms of energy density with other fuels – Fig. 1 [11]. In the case of ammonia, the sufficient compression pressure for its storage is only 10 bar.
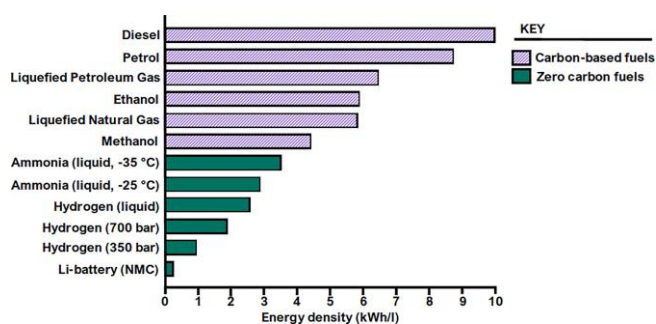

Fig. 1. Energy density comparison for different fuels [11]

Analysis of Table 1 shows that, as in the case of many alternative fuels of non-fossil origin, ammonia requires significantly higher energy to ignite than fossil fuels. This is due to its lower reactivity and flammability. The rate of chemical reaction is the rate at which the reactant is transformed into products. When ammonia is used as a fuel for internal combustion engines, the rate of chemical reactions occurring in the combustion chamber is lower than with traditional hydrocarbon fuels due to the high ignition temperature and low flame speed of burning ammonia. Due to its low reactivity, ammonia has a longer reaction time than most gases. The eddies and turbulences created during the formation of the mixture in the engine combustion chamber have a greater tendency to penetrate the combustion process area, causing the flame to split and its local extinguishing and re-ignition [3]. The calorific value of ammonia is about 40% of the calorific value of conventional hydrocarbon fuels (diesel, petrol, LPG, CNG). The laminar flame velocity during ammonia combustion is also low – about 20% of the laminar flame velocity observed in hydrocarbon fuels. This causes the combustion process to proceed very slowly, which is a problem when using ammonia to power combustion engines because only a part of the injected fuel mixture gets properly burned, which leads to combustion process instability and a drop in thermodynamic efficiency. At the same time, ammonia has a much higher octane number than gasoline and, therefore, a higher resistance to knocking combustion. This allows the use of a high compression ratio

to increase the engine thermal efficiency and/or set high boost pressure to increase the specific power. In addition, ammonia has a high latent heat of vaporization of 1370 kJ/kg. For example, ethanol, liquid hydrogen, and gasoline have latent heat of vaporization of 840, 445.6, and 305 kJ/kg, respectively. This means that if ammonia is injected into the engine combustion chambers, the combustion temperature can be drastically reduced, causing incomplete combustion and reduced engine efficiency. The magnitude of the flame quench distance for a stoichiometric mixture of air and ammonia is about 7 mm, which is about 10 times greater than for hydrogen. This means that heat losses through the combustion chamber walls will be smaller for ammonia. Furthermore, although the calorific value of ammonia is less than half that of typical fossil fuels, the stoichiometric air-fuel ratio for ammonia is also about half that of typical fuels. This means that for the same amount of air intake, the input energy will be similar but with twice the fuel (ammonia) consumption. The production, storage, transportation, and distribution of ammonia are much simpler than for many other fuels (especially hydrogen) [68].

2.1. Ignition delay time

The ignition delay value is critical for assessing fuel combustion process efficiency. It is equivalent to the pre-ignition time of a homogeneous mixture under specific pressure and temperature conditions. The ignition delay value is also a key indicator of the fuel reactivity and combustion reaction, often used in analyzing chemical kinetic mechanisms and predicting flame behavior under specific conditions [3]. Compared to conventional hydrocarbon fuels (e.g. gasoline, diesel oil, methane, etc.), ammonia is characterized by a higher ignition temperature and ignition energy, which is a challenge for practical applications. This requires further research into its combustion characteristics and the development of optimal combustion process strategies.

2.2. Laminar burning velocity

Flames are generated by an irreversible chemical reaction in which the unburned air-fuel mixture is heated and converted into combustion products. Laminar Burning Velocity (LBV) is an important concept in combustion theory. LBV is defined as the velocity of the flame front laminar moving in the direction normal to its surface towards the unburned combustible mixture. The flame spread rate is usually higher for fuels with higher LBV values [3, 13]. LBV contains information relevant to thermodynamics and chemical kinetics, which is essential when studying the

mechanisms of flame propagation in mixtures containing ammonia. The maximum propagation speed of the ammonia flame is about 0.007–0.15 m/s, which is about one-fifth of that of hydrocarbon fuels due to its lower reactivity [5, 6, 48].

2.3. Flame extinction processes

An important issue is the susceptibility of ammonia flames to blow-off under turbulent conditions, which makes the study of their extinction limits important. In the case of a lean mixture, ammonia flames have a higher extinction limit under high turbulence conditions, which is attributed to diffusion-thermal instability. Due to hydrogen diffusion, the blow-off speed of ammonia-hydrogen-nitrogen-air flames significantly exceeds the blow-off speed of methane-air flames. The blow-off limit generally increases with increasing hydrogen fraction in the fuel mixture and air temperature. [30, 59, 78].

3. Fueling internal combustion piston engines with ammonia – challenges

The idea of using ammonia as a fuel for internal combustion engines in road vehicles is not new, and the history of its use, which began at the beginning of the 20th century, was discussed in more detail in [7, 18, 28, 31, 43]. However, ammonia used as a fuel for internal combustion engines poses various problems that need to be solved. In the case of CI engines, the biggest challenges are: high auto-ignition temperature, narrow flammability limits and, in particular, high latent heat of NH_3 vaporization, which causes large temperature drops of the combustible mixture at the moment of ammonia injection, which creates major complications. In turn, the use of ammonia in SI engines is limited by narrow flammability limits and low flame speed, causing incomplete combustion [10, 49]. Fuel can be supplied to the cylinder in two different ways, i.e. via indirect or direct injection of ammonia in the gas phase – Fig. 2. However, in the case of indirect injection, the air supplied to the combustion chamber is displaced, and thus the efficiency of volumetric filling of the engine tends to be reduced. Direct injection of liquid ammonia significantly reduces the temperature in the cylinder due to the high latent heat of ammonia vaporization. This significantly improves the efficiency of volumetric filling because it does not displace the air and cools the mixture [55]. This is beneficial in the case of SI engines. One possible way to improve the efficiency of mixing ammonia with air and thus facilitate its combustion is to create turbulence in the combustion chamber. However, too little swirl does not significantly affect combustion, while too much swirl negatively affects combustion by tearing or blowing off the flame due to its low propagation velocity [12]. The low propagation velocity of the flame makes ammonia more suitable for engines that mostly operate at relatively low rotational speeds [12]. In order to improve the performance of an engine fueled by pure ammonia, numerous studies have examined various aspects such as increasing the ignition energy, multiple ignitions, increasing the compression ratio, supercharging, installing vortex deflectors, increasing the ammonia inlet temperature and the ignition advance angle have been undertaken. However, these measures did not bring sufficient improvement [18, 28, 31, 43]. When ammonia is used in internal combustion engines as a fuel, the chemical reaction rate is slower than in the case of traditional hydrocarbon fuels due to its high ignition temperature and low flame propagation velocity. In summary, the combustion of pure ammonia in spark-ignition (SI) or compression-ignition (CI) engines is difficult due to its generally poor combustion properties [53, 80]. In order to solve the above-mentioned problems resulting from difficult ignition and limitations in the ammonia combustion process, various types of ammonia admixtures acting as combustion promoters were used – Fig. 2 [10].
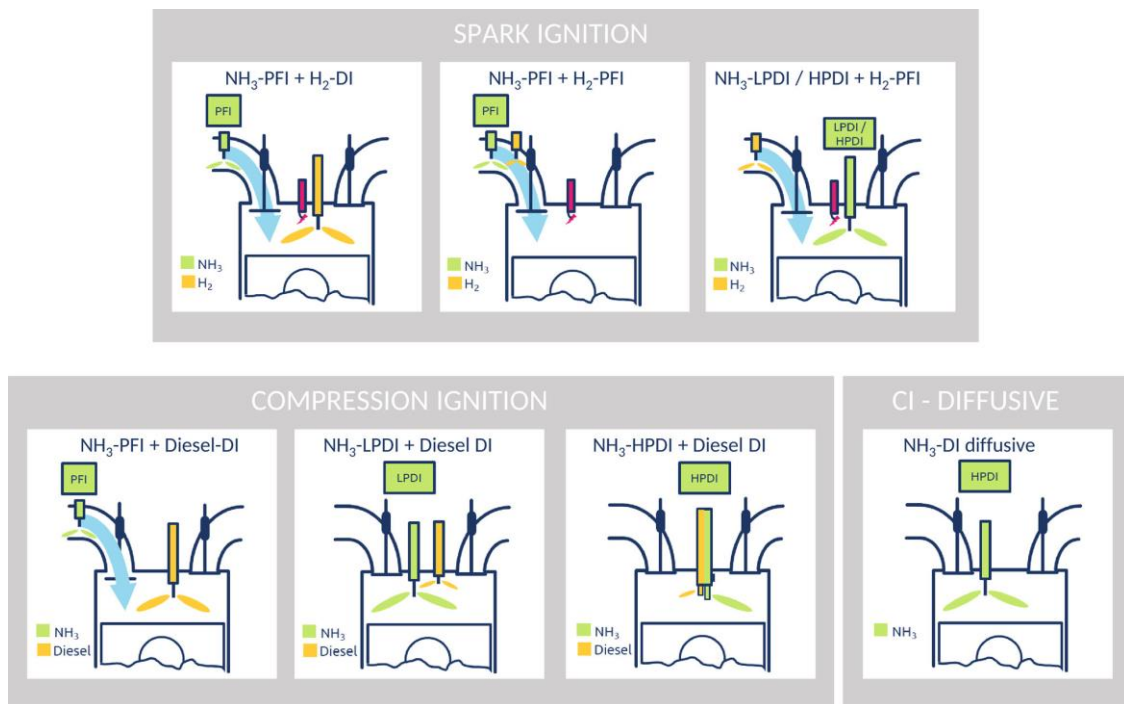

Fig. 2. Combustion concepts for spark ignition engines and compression ignition engines [10]

By using indirect injection into the intake manifold, gaseous ammonia can be supplied to the engine along with air – Fig. 2. Direct injection can also be used, supplying ammonia directly into the cylinder in liquid form, independently of the accompanying fuel supporting the combustion process, which can also be injected directly into the cylinder, e.g. as it is in the case of CI engines – Fig. 2 [12]. Fuel can also be injected into the intake manifold through separate injectors for liquid ammonia and liquid combustion aid fuel – Fig. 2. The fuel supporting the combustion process itself can also be supplied by direct injection into the combustion prechamber [2, 12, 58]. The problem of ammonia ignition is commonly solved by mixing ammonia with traditional fuels such as petrol, diesel oil, LPG, CNG, ethanol, and methanol [29, 32, 81]. Among these options, hydrogen is a particularly preferred combustion promoter [26, 28, 31, 33, 43, 47, 79]. Since traditional fuels ignite at a lower temperature than ammonia, this increases the temperature of the mixture in the cylinder, thus helping to ignite the ammonia [18, 28, 31, 43, 53, 80]. Dimethyl ether (DME) [38, 56, 57], and diethyl ether (DEE) [25, 60] can also be used as combustion promoters. Solutions based on the use of ammonia with combustion promoters is an area of research that requires further development in terms of fuel injection and ignition control and optimization of combustion strategies, as knowledge in this area is limited. To date, about 50 gaseous and liquid combustion promoters added to ammonia have been tested. Research results have proven that hydrogen and acetylene are the two most effective combustion promoters for both SI and CI engines [82]. Currently, the most commonly used promoter in SI engines is hydrogen, which can come from a separate tank and fuel system or on-board ammonia conversion. In such a case, only ammonia is needed as fuel, along with the fuel system for ammonia itself. Ammonia conversion requires a temperature in the reactor of about 400°C. In the case of an on-board reactor, exhaust gases are used for heating, although their temperature is much lower, and therefore, the use of noble metal catalysts is necessary. The lack of carbon in both hydrogen and ammonia eliminates carbon-related emissions. The only emission problems are nitrogen oxides and ammonia, which can be largely removed by means of a modified SCR catalyst [18, 36, 56, 68]. Partial ammonia conversion can bring benefits in improving engine performance, reducing exhaust emissions and reducing the corrosiveness of ammonia to engine components made of brass, copper and nickel. The disadvantage of using hydrogen as an admixture to ammonia is the increased NO_x emission. Hydrogen can also have a negative effect on metal engine components due to the phenomenon referred to as hydrogen embrittlement. Research is also being conducted into the possibility of using gasoline, alkanes or alcohols as promoters of the ammonia combustion process in SI engines. In turn, the nature of compression ignition requires the use of highly reactive fuels such as diesel oil and DME as promoters to initiate ammonia ignition. The most important parameters closely related to the performance and operating characteristics of the engine should be well-optimized. High-performance ignition systems are required. A dedicated injection system and the development of optimal injection strategies may be the most complex components and processes requiring development in ammonia-fueled engines. After introducing combustion promoters, the flexibility of injection increases, and the complexity of fuel supply and injection systems increases significantly [34, 82]. Figure 3 shows the possibilities of using ammonia in various vehicle drive technologies.
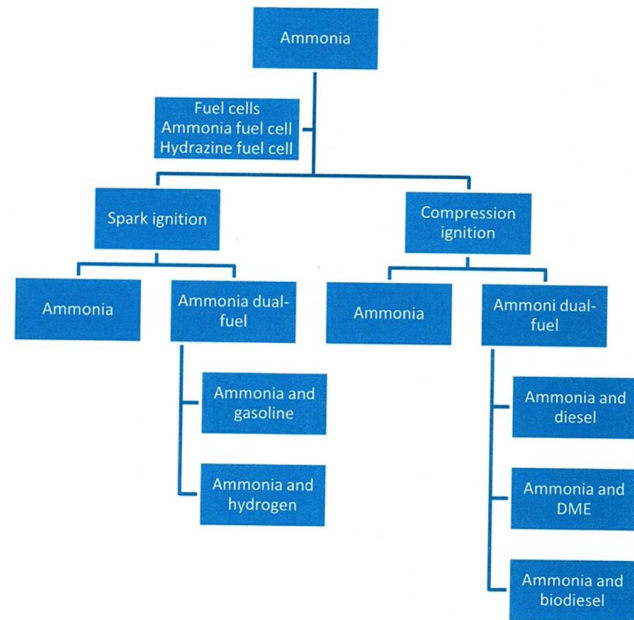

Fig. 3. Possibilities of using ammonia as a fuel for various powertrains [2]

Figure 4 shows the most commonly used mixtures of ammonia with fuels supporting combustion processes in SI and CI engines, along with the parameters influencing the combustion process and engine performance [82].
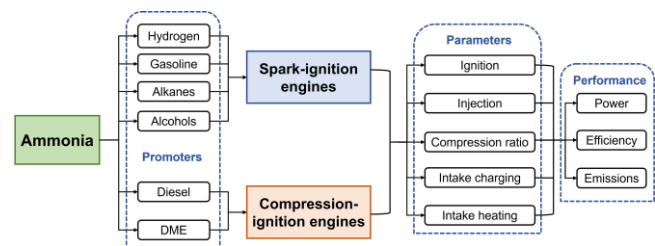

Fig. 4. Directions of development of ammonia mixtures with combustion promoters and main parameters influencing engine performance [82]

Key parameters influencing the combustion process – Fig. 4, closely related to engine performance, should be well optimized. For example, due to the lower speed of the combustion course, the ignition advance angle should be much higher when using ammonia compared to hydrocarbon fuels. The use of high efficiency ignition systems is also important for improving the stability of the combustion process. Designing the right customized fuel injection system and developing optimal injection strategies may be the most difficult issue involved in building (adapting) an ammonia-fueled engine. Even assuming that the engine is powered by pure ammonia, the above issue is additionally complicated by the possibility of supplying the engine with ammonia in the gaseous or liquid phase, and the supply of

ammonia can be performed using indirect injection into the intake manifold or direct injection into the combustion chamber. After introducing combustion promoters into ammonia, the complexity of the problem of developing an optimized fuel injection system increases even more. Other important parameters include compression ratio, boost method and pressure, mixture temperature control, etc. [9, 17–19, 67].

3.1. Ammonia as a fuel for spark ignition combustion engines

Ammonia is mainly used to power SI engines. This is due to its high autoignition temperature and high octane number. The high octane number allows the compression ratio to be increased without the risk of knocking combustion compared to a gasoline-fueled engine, allowing the engine's thermal efficiency to be increased to about 37% [10, 82]. The calorific value of the stoichiometric mixture of ammonia with air is higher than that of the mixture of gasoline with air, but the consumption of ammonia is double that of gasoline due to the low excess air to ammonia ratio (6:1). Only occasionally is ammonia used as a fuel on its own. In most cases, another fuel acting as a combustion promoter is added to ammonia. The most common combustion promoter is hydrogen, but gasoline, ethanol, LPG and natural gas are also used. The results of tests on the use of pure ammonia to power SI engines showed difficulties in engine operation above the speed of about 2000 rpm due to problems in the combustion process caused by difficult ignition, low reactivity of ammonia, unstable combustion process of the mixture, narrow range of ammonia flammability and low speed of laminar flame spread [12]. Slow flame propagation results in the combustion process time getting extended and thus requires changing (optimizing) the ignition advance angle, i.e. the ignition timing relative to the crankshaft rotation. Major difficulties also occur in engine operating conditions in the range of low loads and at variable engine speed and load. As stated, the above problems can be reliably reduced using a high compression ratio, engine supercharging and an ignition system with a high ignition energy (e.g. plasma) [12, 69]. At the same time, it was also noted that the engine could operate smoothly in all conditions after adding a small amount of hydrogen to ammonia as a fuel admixture and a combustion promoter. Another advantage of hydrogen as an admixture to ammonia is that such a fuel mixture will continue to be free of CO_2 emissions. The optimum amount of hydrogen admixture was determined to be between 5 and 10% by volume, which, apart from improving the combustion process, increases the engine's thermal efficiency by up to > 42% and increases its power. A higher share of hydrogen in the mixture with ammonia leads to a decrease in the engine thermal efficiency due to the increase in the amount of heat dissipated through the walls of the engine combustion chamber [36, 42, 45, 51, 56]. Moreover, the addition of H_2 to NH_3 reduces the emission of unburned NH_3 [37]. The influence of various parameters on the performance of the SI engine fueled with $NH_3/NH_3 + H_2$ was shown in Fig. 5.
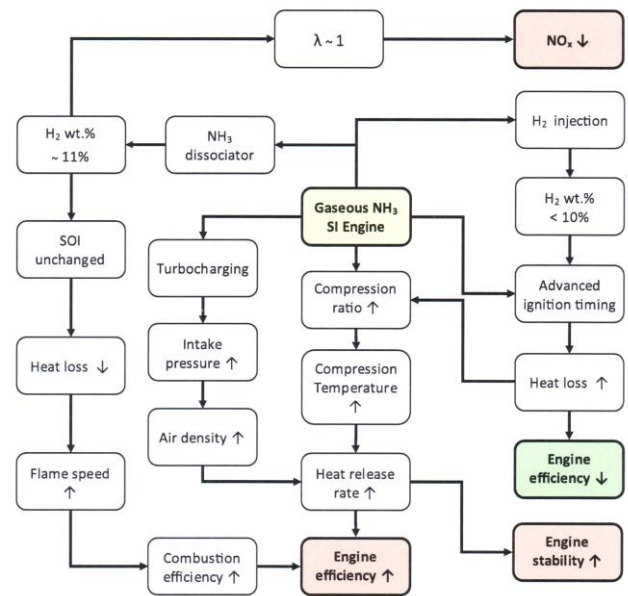

Fig. 5. Parameters influencing the operation of a SI engine fueled by NH_3 or $NH_3 + H_2$ mixture [11]

For existing SI engines fueled with ammonia, gasoline is often used as the second fuel (supporting the combustion process as a promoter). Such a "dual-fuel" engine fueled with both ammonia and gasoline also allows the engine to operate only on gasoline, which is beneficial because studies have shown that the operation of an ammonia-fueled engine at idle speed tends to be very unstable [20, 22]. In addition, the presence of ammonia significantly increases the octane number of the fuel mixture, resulting in a significantly greater resistance to knocking combustion, which, by increasing the compression ratio, allows for improved engine thermal efficiency. Additional benefits in such a case can be brought by the use of liquid ammonia injection into the engine intake manifold. Ammonia in the liquid phase does not displace as much air as in the case of the gas phase and, through its evaporation, cools the prepared combustible mixture, allowing a higher density dose to be delivered to the cylinder. However, this causes a significant reduction in the temperature of the mixture during compression, along with its greater inhomogeneity and makes the subsequent ignition and combustion process more difficult.

3.2. Ammonia as a fuel for compression ignition combustion engines

Because of ammonia's low reactivity, very high autoignition temperature and very low cetane number (21), spontaneous ignition of a stoichiometric ammonia mixture is extremely difficult. Experimental results [70] proved that a compression ratio of at least 40:1 or more is required to achieve ammonia auto-ignition by compression without preheating the intake air. Even when the inlet air is heated to 148°C, a compression ratio of 35:1 is required for spontaneous ammonia combustion [24]. Such high compression ratios result in increased heat loss due to the high surface-to-volume ratio of the combustion chamber and friction losses that can compensate for the increase in thermal efficiency achieved by the increased compression ratio. Attempts have also been made to aid the ignition of ammonia

by using high-energy spark plugs, glow plugs and special high-temperature glow coils. However, these experiments have been unsuccessful [24]. In other studies [61], attempts were made to support the liquid ammonia ignition process in a CI engine by using spark plugs. A satisfactory result of both ignition and combustion was achieved at compression ratios in the range of 16:1–24:1. The highest engine efficiency value achieved was at the injection advance angle of 150–180 BTDC for liquid ammonia. The maximum engine power achieved was 10% lower than the power of the engine fueled with diesel oil. The stoichiometric air to fuel-ammonia ratio was 6.0466 compared to 14.322 in the case of diesel oil. This indicated a lower energy density of ammonia, which can be compensated by injecting a larger fuel dose into the cylinder with the prepared mixture, thus achieving an energy density comparable to the stoichiometric air to diesel mixture [31].

Finally, to meet the challenges related to the difficult combustion process of pure ammonia as a fuel, as in the case of SI engines, a fuel admixture is used as a combustion promoter. In the case of SI engines, fuels with a higher cetane number are preferred for use with ammonia due to their better ignition properties. The most commonly used combustion promoters are: H_2, diesel fuel, DME, DEE, and biodiesel [28, 45]. In the case of using ammonia with an admixture in the form of some other fuel as a combustion promoter, the engine performance depends to a large extent on the cetane number of this added fuel with a higher cetane number, which increases the engine performance by shortening the ignition delay and improving the overall combustion efficiency [14, 35, 54]. The effects of various operating parameters on the performance of an SI engine fueled with NH_3 have been shown in Fig. 6.
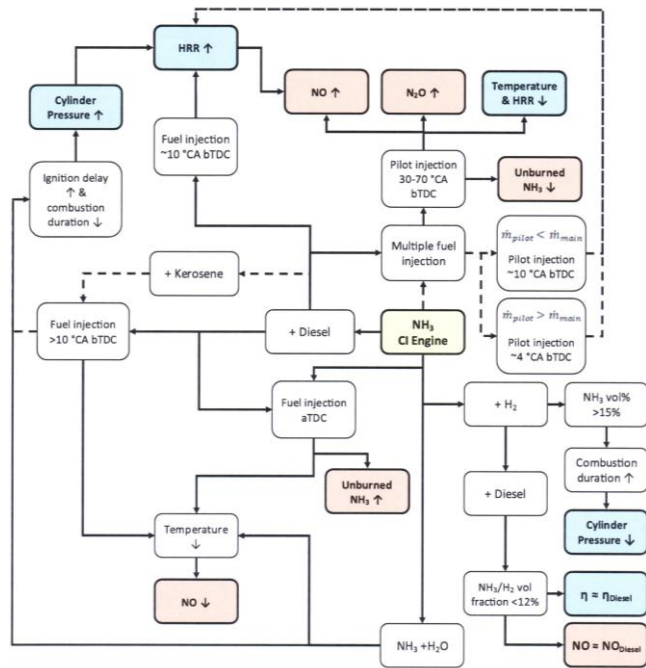

Fig. 6. Parameters influencing the operation and performance of a CI engine fueled with NH_3 [11]

4. Exhaust emissions of combustion engines fueled with ammonia

Ammonia combustion produces mainly NO as a harmful combustion product, with minor traces of NO_2 and nitrous oxide N_2O. These molecules are precursors of acid rain, photochemical smog and the greenhouse effect, especially N_2O. Although NO is not hazardous in the environment, it oxidizes relatively quickly to NO_2 in the atmosphere and is a major pollutant of concern in many cities. NO_2 can cause allergic reactions and lung dysfunction. N_2O is also an undesirable emission because of its strong greenhouse effect, about 300 times greater than CO_2. In general, nitrogen oxide (NO_x) emissions are one of the main problems to be solved in the development of ammonia-based fuel technologies. Ammonia, due to its low reactivity, has a longer reaction time than most gases used as fuel. As a result, during the process of creating the mixture and then its combustion, the eddies and turbulences that are created have a greater tendency to affect the combustion process, causing the flame's local extinction and re-ignition, resulting in flame interruption [73]. It has been shown that methane can burn continuously at an air flow rate about twice as high as in the case of ammonia in a much wider range of excess air coefficients than ammonia [72]. The laminar flame propagation speed when burning NH_3 is much lower than in the case of H_2 and CH_4 [32]. It is, respectively, at the stoichiometric excess air coefficient for NH_3 ~7 cm/s, while for CH_4 ~37 cm/s, and for H_2 ~291 cm/s [32, 39]. Ammonia requires a higher ignition temperature and results in a lower flame propagation velocity. From the point of view of emissions, N_2 has a dominant effect on the formation of NO in the stoichiometric combustion of NH_3 in air. Due to the low reactivity of N_2, the thickness of the flame preheating zone for NH_3 is an order of magnitude greater compared to the combustion of methane under stoichiometric conditions. In contrast to methane, NO increases rapidly in the zone preheated by the flame front of combusting NH_3 instead of in the post-ignition zone, which indicates that the dominant route of NO formation is due to decomposition and not thermal during NH_3 combustion [39]. A major problem of ammonia-fueled engines is the emission of unburned ammonia resulting from the low flame propagation velocity, and therefore, slow combustion process, and the large flame quenching distance, which leads, for example, to unburned ammonia remaining in the volume of the combustion chamber gaps. When hydrogen is used as a promoter of the ammonia combustion process, the main pollutants emitted are NO_x, NH_3 and N_2O. Most of the NO_x produced in the combustion process of ammonia and hydrogen is nitrogen oxide (NO) and a small amount of nitrogen dioxide (NO_2) [40]. When a small amount of hydrogen is added to ammonia, the combustion temperature increases, which promotes the formatting of NO_x through thermal processes. As a result, engines fueled with ammonia with a hydrogen admixture emit more NO_x than engines fueled with pure ammonia. This becomes more and more apparent with the increase of the hydrogen content in the fuel, especially in the case of lean mixtures [36, 37, 41]. During the course of the lean mixture combustion process, NO_x emissions can reach levels above 5000 ppm. However,

in the case of rich mixtures with insufficient oxygen for complete combustion, NO_x generation is lower due to thermal and fuel decomposition processes [36, 37]. The NO_x emission level is also influenced by various engine operating parameters. For example, by changes in the compression ratio [44], engine speed [15] and ignition timing (advance angle) [77]. These cause an increase in the peak temperature in the engine cylinders, generally leading to increased NO_x emissions. However, the size of the engine load shows a different pattern. In the conducted studies [36] it was found that an increase in the intake pressure of the mixture caused higher NO_x emissions in the case of a lean mixture, while a slight decrease was observed in the case of stoichiometric and rich mixtures.

In the case of unburned ammonia emissions, two main sources of its origin can be distinguished, both related to flame extinction. The first source is unburned ammonia trapped in the crevices of the combustion chamber, and the second is unburned ammonia remaining as a result of extinguishing the combustion process near the cold surfaces of the combustion chamber [72]. Therefore, factors that affect maximum engine cylinder pressure and flame extinction, such as the amount of hydrogen in the ammonia mixture, the compression ratio (temperature) and the excess air ratio [40, 44, 66], can lead to changes in NH_3 emissions. The effect of these factors on NH_3 emissions is usually opposite to their effect on NO_x emissions, requiring a compromise to be found to achieve a balance between NH_3 and NO_x emissions [37, 40]. The conducted studies have shown that adding hydrogen to ammonia increases the pressure in the cylinder and strengthens the mechanism of the unburned ammonia occurrence in gap spaces, but at the same time, it can significantly reduce the ammonia flame quenching distances and contribute to the reduction of the total amount of ammonia emissions. The combustion of pure ammonia can lead to the concentration of ammonia in the exhaust gases of up to 3%, and the introduction of 15% hydrogen can significantly reduce the amount of this emission to about 1% [44]. N_2O emissions can account for 3–8% of total GHG emissions from CI engines equipped with DOC/DPF/SCR aftertreatment systems and can reach as high as 8.3% in urban driving conditions [52]. N_2O emissions from an engine fueled by hydrogen-doped ammonia are higher because N_2O can also be produced by burning ammonia. Although the magnitude of N_2O concentration (usually around 100 ppm [40]) in the exhaust gas is much smaller than NO_x. The magnitude of N_2O emissions and its control is a major challenge and problem due to its very strong greenhouse effect (about 300 times greater than CO_2) [77]. During the combustion of an ammonia-hydrogen mixture, N_2O production decreases with increasing hydrogen content in the mixture, but at the same time, the amount of unburned ammonia increases. When hydrocarbon fuels are added to ammonia as combustion promoters, unburned hydrocarbons, carbon monoxide, and soot (diesel engines) constitute additional emissions. Therefore, considering ammonia-hydrocarbon fuel mixtures and combustion of the lubricating oil entering the engine combustion chambers, eight types of emissions, including NH_3, NO, NO_2, N_2O, HC, CO, CO_2 and soot should be taken into account when

considering this solution. As a result, as in the case of piston combustion engines powered by conventional hydrocarbon fuels, exhaust aftertreatment systems are necessary. In the case of NO_x reduction, the most effective solution currently is using three-way catalytic converters coated with rhodium, platinum and palladium and selective catalytic reduction converters based on small-pore zeolites. Three-way catalysts are usually used in engines operating at stoichiometric air-to-fuel ratios, while selective catalytic reduction converters are mainly used in low-emission combustion engines. Previous research results on the effectiveness of using three-way catalysts for the aftertreatment of exhaust gases from a SI engine fueled with ammonia with an admixture of gasoline as a combustion promoter have shown the effectiveness of this solution in reducing CO, HC, NH_3 and NO emissions during engine operation on a mixture close to stoichiometric [23]. However, when lean mixture combustion is required, the use of a three-way catalyst is not effective enough. In this case, selective catalytic reduction converters become more appropriate, especially for reducing NO_x emissions. In the case of using ammonia-based fuel, the selective catalytic reduction system uses ammonia directly as a reducing agent. While in the case of engines fueled with conventional hydrocarbon fuels, an aqueous urea solution is used for the operation of the selective catalytic reduction system, from which ammonia is obtained. The most effective recommended method for reducing the volume of ammonia emissions is the use of an ammonia slip catalyst, which selectively oxidizes unburned or re-generated NH_3 in the engine exhaust to N_2. There are three different processes and mechanisms of ammonia oxidation: the NH mechanism, the N_2H_4 mechanism, and the i-SCR mechanism. In the case of the NH mechanism, adsorbed NH_3 is first converted to NH by two-step hydrogen dissociation, and then NH is oxidized to HNO, which reacts with NH to form N_2 and H_2O. This mechanism is applicable to systems containing noble metal catalysts (such as Ag and Pt, etc.) [21, 75]. The N_2H_4 mechanism, also described as the hydrazine mechanism, involves the dissociation of NH_3 to form NH_2, followed by the reaction of the two NH_2s to form N_2H_4. N_2H_4 is then re-oxidized by O_2, forming N_2 and by-products such as NO_x. This mechanism is used for aftertreatment systems using transition metals [4]. The mechanism of i-SCR is that NH_3 is first oxidized to NO and then reduced to products such as N_2 and N_2O by NH_3 due to the reaction going on in SCR [50, 74]. Based on the above analysis, in the case of using compression ignition assisted by spark ignition of ammonia with hydrogen admixture, an example of an exhaust aftertreatment system should include all elements, as shown in Fig. 7 [51].

5. Lubrication of ammonia fueled internal combustion piston engines – challenges

Ensuring reliable engine operation throughout its entire service life requires the development of an appropriate lubrication system and a lubricant compatible with the fuel used. Challenges related to the combustion of pure ammonia or ammonia with a small admixture of another fuel, such as high ignition energy, the low flame propagation speed of the burning air-fuel mixture in the engine combus-

tion chambers, slow combustion reaction kinetics or NO_x formation, all favor the presence of chemically active substances in the form of unburned NH_3, O_2 and NO_x in the gases seeping into the engine crankcase.
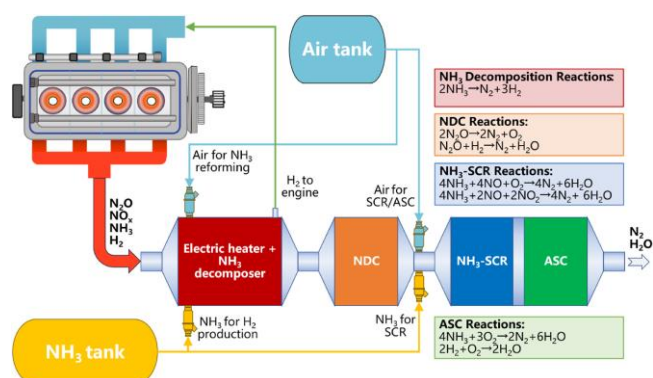

Fig. 7. Example of an exhaust aftertreatment system for a compression ignition assisted by spark ignition of ammonia with a hydrogen admixture [53]

Therefore, interactions between ammonia combustion products and lubricating oil are to be expected, which, if poorly selected, can adversely affect the efficiency and quality of lubrication. So far, very little research has been done on the impact of combustion products of fuel whose main component is ammonia, on lubricating engine oil [1, 7, 8, 46, 62, 63]. In terms of determining changes in the physicochemical properties of lubricating oil during operation, the conducted studies [46] question the representativeness of TBN and TAN measurements as indicators of the level of lubricating oil degradation expected in ammonia-fueled combustion engines. Therefore, additional studies are necessary to identify the mechanisms related to the impact and reliable measurement of the impact of ammonia on the degradation processes of lubricating oil used in ammonia-fueled combustion engines. During the operation of engines primarily fueled with ammonia, an increase in exhaust gas blow-by into the engine crankcase was also observed, which was associated with the observed adhesive wear at the contact of the interacting surfaces of the ring/piston/cylinder. The scope of this wear depended on the oil used to lubricate the engine. Hence, a hypothesis was put forward that ammonia reduces the oil film thickness on the cylinder wall, which may cause periodic occurrences of semi-dry friction [46]. The engine studies showed different amounts of wear of the piston-cylinder assembly depending on the oil composition at their same viscosities. This observation indicated that ammonia can affect the chemical composition of oil additives and limit their ability to form protective layers on the metal surface to prevent wear. Furthermore, ammonia can have a strong corrosive effect on the alloys bearing in copper. Therefore, it is necessary to conduct extensive, multidirectional work to identify the potential interactions between ammonia fuel without and/or with admixture of other fuels and engine lubricating oils. In addition, in order to determine the effect of ammonia on the tendency of lubricating engine oil to form deposits, the oil sample was subjected to reactive gas treatment

with ammonia [46]. The tendency of lubricating oil to form deposits was studied both under static and dynamic conditions. Static conditions corresponded to e.g. an oil pan, and the dynamic to e.g. the area of interaction of piston rings with cylinder liner in a combustion engine. It was found that even a trace admixture of NH_3 in lubricating oil caused a significant increase in the tendency of lubricating oil to form deposits under both static and dynamic conditions [46]. This was a surprising observation, considering that lubricating oils exposed to air-NH_3 mixtures showed less oxidation than those exposed to air alone without ammonia [1, 46, 62]. This indicates that NH_3 influenced the tendency of the lubricating oil to form oil deposits in a way that was not consistent with the results of conventional physico-chemical analyses of the oil properties.

6. Conclusions
− The properties of ammonia as a carbon-free chemical compound with a high hydrogen content its ease of storage and transport make it easy to meet the ecological requirements as a fuel for internal combustion piston engines in the era of carbon neutrality.
− The greatest challenges associated with the use of ammonia as a fuel include: high autoignition energy, low laminar combustion flame velocity, slow combustion reaction kinetics and the presence of active chemical compounds in the exhaust gases, such as: unburned NH_3, and NO_x.
− Combustion of ammonia with a high cetane number and a combustion promoter with a low autoignition temperature is a possible solution the problem of difficult ignition and combustion of pure ammonia.
− The results of previous studies have shown interactions between the components of ammonia-containing fuel and lubricating oil, which adversely affect the physico-chemical and functional properties of the lubricating oil.
− The mechanisms of lubricating oil degradation in the presence of ammonia are still unclear and differ from those observed in their reaction with hydrocarbon fuels.
− Excessive wear of key engine components has been identified as a key challenge for newly developed lubricants dedicated to ammonia-fueled engines. In addition, ammonia can have a strong effect on the corrosion of copper containing bearing alloys. Increased wear in the piston ring area is probably related to the effect that ammonia has not yet fully explained on the oil film covering the friction surfaces of the interacting engine components.
− The proper cooperation between ammonia and engine lubricant is of great importance for ensuring reliable engine operation throughout its service life.
− The effect of ammonia on the performance of lubricating oil depends on its composition. This creates an opportunity to develop engine oil technologies adapted to the lubrication of ammonia-fueled engines. That is, oil with improved properties in terms of controlling wear of interacting engine parts and the tendency to form harmful deposits.

Nomenclature

BTDC	before top dead center	LBV	laminar burning velocity
CI	compression ignition	LPG	liquefied petroleum gas
CNG	compressed natural gas	ON	diesel fuel
DEE	diethyl ether	PM	particle matter
DME	dimethyl ether	SCR	selective catalytic reduction
DOC	diesel oxidation catalyst	SI	spark ignition
DPF	diesel particulate filter	TAN	total acid number
EU	European Union	TBN	total base number
ICE	internal combustion engine		

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