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Assessment of the measurement capabilities of hydrogen and ammonia mixture combustion in a TJI engine

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The combustion of carbon zero-emission fuels such as hydrogen and ammonia is one of the key directions in the search for alternatives to fossil fuels. Co-combustion of these fuels is possible through the use of active two-stage combustion system. This article presents the methodology for fuel preparation and the design of fuel supply systems for an internal combustion engine intended for railway traction applications. The physicochemical properties of hydrogen and ammonia are discussed, along with their combustion potential in a TJI-type engine. Methods for storage and supply of hydrogen and ammonia to the engine are presented, and a review of flow meters suitable for these fuels is provided, including limitations resulting from their specific properties. Approaches for preparing hydrogen-ammonia mixtures for combustion studies are described, including the determination of air demand for various H_2+NH_3 *mixture compositions. The article concludes with an analysis of typical emission levels of nitrogen oxides and ammonia for different ammonia combustion strategies and for ammonia-hydrogen co-combustion.*

1. Introduction

Current efforts to eliminate emissions generated by the transport sector include not only energy generation from renewable energy sources, but also its storage and utilization. Environmentally friendly and efficient energy carriers include hydrogen and ammonia. These gases can be used as carbon-free fuels, but their application is associated with several challenges. The low density, low boiling point, and high condensation pressure of hydrogen make its storage and transportation difficult [9]. Therefore, the use of ammonia as a hydrogen carrier appears promising, as the production, storage, and transport of this compound are already well established industrial processes. Another important aspect is the application of these fuels in internal combustion engines for railway traction. The main limitations of ammonia are its low reactivity and slow flame propagation during combustion. In contrast, hydrogen is highly reactive, and its combustion is characterized by a high flame front temperature and high flame propagation speed.

Considering the characteristic properties of both compounds, their combination appears to be a particularly promising solution, enabling the exploitation of their advantages while mitigating many of their individual drawbacks as future fuels.

2. Combustion of hydrogen and ammonia

2.1. Physicochemical properties of hydrogen and ammonia

Hydrogen and ammonia are gaseous fuels that can enable the decarbonization of transport in the future energy transition. Both compounds can be used for energy generation in fuel cells or in appropriately adapted internal combustion engines for railway traction. However, despite this common application potential, hydrogen and ammonia differ significantly in their physicochemical properties. These differences also result in distinct combustion characteristics.

Hydrogen is the lightest chemical element and exists under standard conditions as a colorless, odorless, and non-toxic gas. It exhibits an exceptionally high

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lower heating value of approximately 120 kJ/g. However, its low density, very low liquefaction temperature, and high permeability through microscopic leaks make hydrogen storage technically challenging.

These limitations are less pronounced for ammonia. The gaseous density of ammonia is nearly nine times higher than that of hydrogen, and it can be stored in liquid form under conditions that are significantly easier to achieve than those required for hydrogen.

Another key difference between these gases is thermal conductivity, which is substantially lower for ammonia. Significant differences are also observed in kinematic viscosity and specific heat capacity values.

Table 1. Properties of hydrogen and ammonia [18, 19]

Physical quantity	Unit	H_2	NH_3
Molar mass	g/mol	2.016	17.03
Density	kg/m^3	0.4128	3.673
Specific heat capacity (Cp)	J/(kg·K)	14320	2288
Specific heat capacity (Cv)	J/(kg·K)	10190	1672
Thermal conductivity	W/(m·K)	0.1763	0.02855
Dynamic viscosity	Pa·s	$8.83 \cdot 10^{-6}$	$1.03 \cdot 10^{-5}$
Kinematic viscosity	m^2/s	$2.14 \cdot 10^{-5}$	$2.81 \cdot 10^{-6}$
Boiling point	K	20.3	239.7

2.2. Combustion characteristics of hydrogen and ammonia

The key parameters used to characterize fuel combustion are LFS and IDT. Laminar Flame Speed (LFS) defines the velocity at which the laminar flame front propagates, typically expressed in cm/s. Ignition Delay Time (IDT) represents the ignition delay, defined as the time interval between the application of ignition energy and the actual onset of combustion. Start of combustion is commonly identified by a rapid increase in pressure and temperature.

Other important combustion-related parameters include the Minimum Ignition Energy (MIE), the Adiabatic Flame Temperature (AFT), and the Heat of Combustion (HoC) [21].

Hydrogen offers several advantages as a fuel. It is highly reactive, as indicated by low values of IDT and MIE, and its flame propagates very rapidly, resulting in a high LFS. However, its application is challenging, mainly due to the high pressure rise following ignition and the very high flame front temperature. These combustion characteristics of hydrogen promote knock-prone operation and lead to elevated NO_x emissions [20].

An additional challenge associated with the use of hydrogen concerns its storage and the proper selection of materials resistant to hydrogen embrittlement.

The existing limitations of hydrogen, including its strong tendency toward knock and the challenges associated with its storage, motivate the consideration of other carbon-free fuels, one of which is ammonia. The combustion behavior of ammonia is nearly opposite to that of hydrogen. Ammonia is characterized by a long ignition delay and slow flame propagation, reflected by a low LFS [21].

From an emission reduction perspective, the lower flame front temperature during ammonia combustion compared to hydrogen is advantageous. This leads to a reduction in nitrogen oxide formation via high-temperature mechanisms. However, due to the long ignition delay and low flame propagation speed, ammonia combustion promotes the emission of unburned NH_3 and reactive radical species.

Considering the contrasting combustion characteristics of hydrogen and ammonia, the use of their mixture as a fuel appears promising. Such an approach enables improved combustion performance, mitigation of knock tendency, and potentially reduced emissions of harmful exhaust components. During the combustion of both fuels, water vapor is formed, while nitrogen-containing species such as NO, NO_2, and N_2O are also generated.

3. Turbulent Jet Ignition engine

3.1. Limitations of spark-ignition engines

Conventional spark-ignition engines exhibit several limitations, including, among others:

- limited lean-burn capability
- limitations related to flame propagation speed and flame front geometry
- occurrence of knock combustion.

The first limitation results from the difficulty of reliable ignition initiation using conventional spark plugs at very lean mixture. The second is associated with flame front propagation originating from the spark plug, that is, from the center of the combustion chamber, and developing in a hemispherical shape. Knock combustion occurs when the unburned charge undergoes autoignition before being consumed by the propagating flame front.

Modern internal combustion engines are already adapted for hydrogen combustion (Fig. 1). Several manufacturers currently offer hydrogen-fueled internal combustion engines suitable for railway traction applications, including the Cummins X15H [3], Hyundai XH12 [7], and Deutz 7.8 H_2 [4], among others. These hydrogen engines typically operate at an excess air ratio of $\lambda = 1$, which results in limited capability to suppress knock combustion.

These limitations prevent the achievement of higher thermal efficiency and, consequently, hinder reductions in fuel consumption and exhaust emissions.

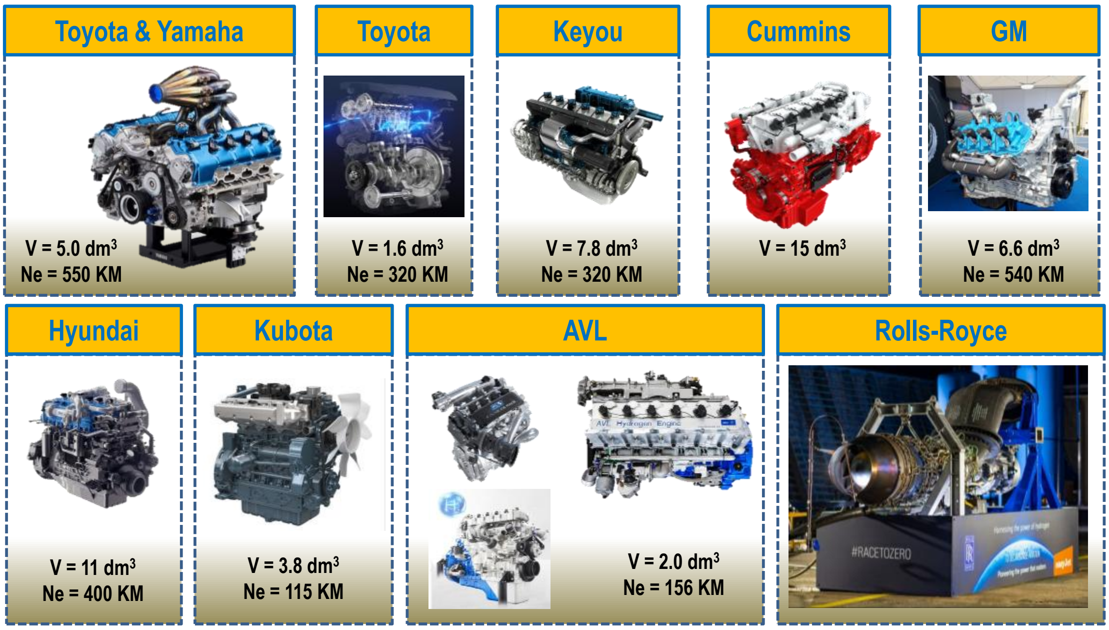

Fig. 1. Hydrogen-fueled internal combustion engines (partially intended for railway traction applications) (based on [1, 3–5, 8, 12, 13, 23])

3.2. Construction of the TJI engine

The TJI combustion system operates on a two-stage combustion concept. The initial combustion processes take place in the pre-chamber and subsequently propagate into the main combustion chamber (Fig. 2).

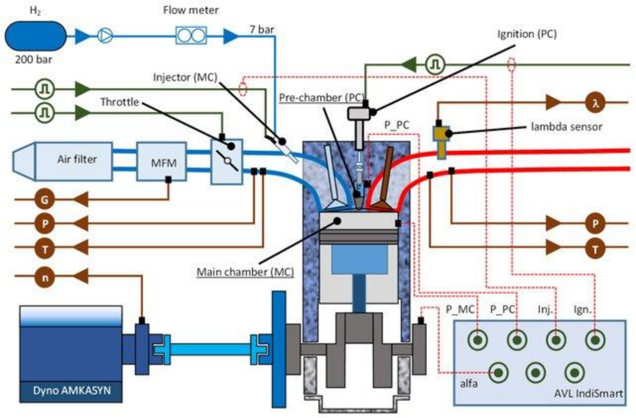

Fig. 2. Schematic of the TJI engine design and measurement instrumentation [20]

The main combustion chamber in conventional spark-ignition engines does not differ significantly from that used in engines equipped with the Turbulent Jet Ignition system. The key difference is the presence of a pre-chamber in TJI engines, which houses the spark plug and may also contain a fuel injector. The pre-chamber is connected to the main chamber through a set of nozzles that enable air flow and flame propagation. Two types of TJI systems can be distinguished:

- Active – the pre-chamber is equipped with additional fuel injection system; this solution is used, among others, in Formula 1 engines
- Passive – no fuel injector is present in the pre-chamber; this type of system is implemented in the Maserati MC20, although an additional spark plug is located in the main combustion chamber.

3.3. Lean mixture combustion in a TJI engine

Lean mixture combustion represents one of the key development directions for internal combustion engines due to its potential to improve thermal efficiency and reduce fuel consumption and exhaust emissions. In conventional spark-ignition engines, lean combustion is limited by difficulties in reliable ignition initiation. However, the TJI system enables stable lean operation due to its specific design.

Ignition is initiated in the pre-chamber, where a rich mixture, close to stoichiometric conditions, is present. The flame then propagates into the main combustion chamber, which contains a lean mixture. This results in multipoint ignition of the charge in the main chamber through turbulent jets of the propagating flame, leading to stable and efficient combustion [20].

4. Methods for forming H_2–NH_3 mixtures

4.1. Hydrogen and ammonia storage in the context of engine system

Supplying an engine with a hydrogen–ammonia fuel mixture requires storage of both fuel components:

- in a single tank or in separate tanks
- in liquid or gaseous form.

Storing an H_2+NH_3 mixture in a single tank eliminates issues related to the formation of a mixture with a precisely defined composition. The fuel components are prepared and blended during tank filling; therefore, the mixture composition is fixed. However, the use of a single tank introduces clear limitations, most notably the lack of flexibility to vary the concentrations of individual components. Another drawback of this solution, directly related to the application of a TJI engine, is the inability to separate the fuel components, for example to enable the injection of pure hydrogen into the pre-chamber.

The use of at least two separate tanks, one for hydrogen and one for ammonia, allows continuous control of the mixture composition, for example by throttling the flow of one of the fuel components. A major drawback of this approach, particularly relevant from an experimental research perspective, is the difficulty in forming a mixture with a precisely defined and reproducible composition.

Both hydrogen and ammonia can be stored in either gaseous or liquid form:

- Gaseous hydrogen is stored under high pressure, typically in the range of 20–70 MPa. Even under these conditions, its volumetric energy density remains low and reaches approximately 5.6 MJ/dm^3 at 700 bar [10].
- Liquid hydrogen storage requires cryogenic cooling and maintaining a temperature of −253°C. The high energy demand associated with cooling makes this storage method significantly less universal and cost-effective, although it provides a higher energy density compared to compressed hydrogen.
- Ammonia can be stored in gaseous form at much lower pressures than hydrogen, typically up to approximately 10 bar [14].
- The boiling point of ammonia is −33.3°C at atmospheric pressure. As a result, the energy consumption required for cooling ammonia storage tanks is significantly lower than that required for liquid hydrogen storage. In addition, the volumetric energy density of liquid ammonia is approximately 11.5 MJ/dm^3, which is higher than that of hydrogen, but still considerably lower than that of gasoline, which ranges from 32 to 34 MJ/dm^3.

4.2. H_2+NH_3 mixture formation using separate tanks

Mixing ammonia and hydrogen requires the use of dedicated mixing systems that prevent the risk of backflow of one gas into the storage tank of the other. Ammonia exhibits strong corrosive properties, particularly toward metals such as copper and zinc, whereas hydrogen can cause hydrogen embrittlement, especially in steels. For this reason, it is essential to protect the fuel supply system against cross-contamination of the gases, especially when one of the storage tanks is not resistant to the chemical effects of the other fuel component.

These challenges are further intensified by the significantly different physical properties of hydrogen and ammonia, most notably by their large difference in density [18, 19].

4.3. H_2+NH_3 mixture formation via ammonia decomposition

It is possible to form an H_2+NH_3 mixture, or even pure hydrogen, through ammonia decomposition. This approach may rely on a single storage tank containing only NH_3. Hydrogen release via ammonia decomposition occurs at relatively low pressure, up to approximately 10 bar, and at high temperatures in the range of 400–800°C, according to the reaction $2NH_3 \rightarrow N_2 + 3H_2$. The process is endothermic (ΔH_r = 46.2 kJ/mol) and is promoted by catalysts such as nickel, ruthenium, or cobalt.

Although this method is advantageous from the perspective of storing ammonia instead of hydrogen, it has several drawbacks. Maintaining the temperature required for the endothermic NH_3 decomposition reaction involves high energy consumption and, consequently, high operating costs, further increased by the need for catalytic materials. In addition, obtaining pure hydrogen or an H_2+NH_3 mixture with a precisely defined composition is very difficult and may require particularly high temperatures and low pressures [16, 17].

4.4. Multi-tank storage and utilization concepts

The use of a single tank containing an H_2+NH_3 mixture prevents separation of the fuel components for the purpose of injecting pure hydrogen into the pre-chamber. However, employing a tank with a mixture of fixed composition eliminates the issues related to mixture formation discussed in Section 4.2.

An optimal solution would therefore involve the use of a tank with pure hydrogen and a second tank containing a hydrogen–ammonia mixture. Hydrogen could be supplied exclusively to the pre-chamber, while the gas mixture would be directed to the main combustion chamber. Hydrogen combustion produces a rapidly propagating flame with a high temperature, which favorably enhances ignition of the charge in the main chamber.

5. Methods for measuring the flow of an H_2+NH_3 mixture

5.1. Fundamentals of fuel mass flow measurement

To conduct combustion studies of an H_2+NH_3 mixture, as well as of any other fuel, in an engine, accurate measurement of fuel consumption is required. Measuring this quantity using thermal or mass flow meters is the most practical approach to achieve this objective. Determining the mass of the gas mixture supplied to the engine over a given time interval does not require additional conversions accounting for parameters such as density, which varies with temperature and pressure. Knowledge of the fuel consumption enables the calculation of further engine parameters, including thermal efficiency and specific fuel consumption.

5.2. Types of flow meters

Measurement of the mass flow rate of hydrogen and ammonia can be performed using several types of flow meters, including:

– **Thermal flow meters** – the measurement is based on the phenomenon of thermal dispersion caused by the gas flowing around the sensor. This method relies on measuring the electrical power required to maintain a constant temperature difference between a heated temperature sensor and a reference sensor measuring the actual gas temperature. Two measurement approaches are applied: either a constant temperature difference is maintained by adjusting the heating power, or a constant heating power is applied and changes in the temperature difference between the heated and reference sensors are measured. The measurement results obtained with thermal flow meters may be affected by several factors, including viscosity, specific heat capacity, and thermal conductivity. This issue is particularly significant for hydrogen, which exhibits a high thermal conductivity of approximately 0.185 W/(m·K). For comparison, the thermal conductivity of CO_2 is about 0.017 W/(m·K). While the high thermal conductivity of hydrogen complicates measurements using standard thermal flow meters, modern designs exist that enable precise mass flow measurement of hydrogen and other media with very high thermal conductivity. An important advantage of this type of flow meter is its low measurement inertia, which ensures high accuracy under rapidly changing flow conditions [22].

– **Coriolis flow meters** – mass flow meters are also referred to as Coriolis flow meters due to the physical effect used for measurement. The sensor contains U-shaped measuring tubes that are excited to vibrate at their resonant frequency by an actuator (Fig. 3). As the fluid flows through the tube, its inertia induces tube deformation, while the Coriolis force causes the inlet and outlet sections of the tube to vibrate in opposite directions, which is detected by sensors. This phenomenon is known as phase shift and its magnitude increases with increasing mass flow through the measuring tube.

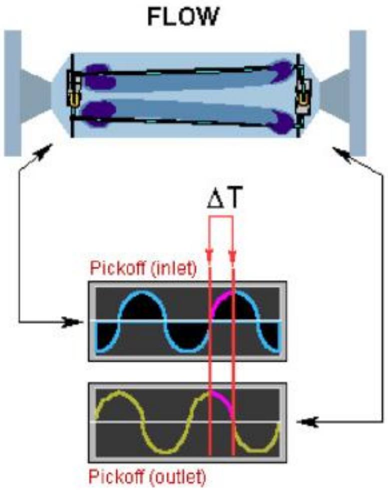

Fig. 3. Operating principle of a Coriolis flow meter [6]

Using this type of flow meter allows for direct measurement of both density and viscosity. However, the application of Coriolis flow meters for hydrogen flow measurement is limited by reduced accuracy at low flow rates. With a properly selected device and an acceptable measurement error of approximately 2%, it is possible to measure a minimum mass flow rate of about 1.8 kg/h. [22].

– **Vortex flow meters** – these devices are based on the formation of vortices known as the Kármán vortex street, which is independent of the type and composition of the fluid flowing around an obstacle placed transverse to the flow direction. The generated vortices induce periodic changes in pressure and flow velocity, which are detected by sensors, such as ultrasonic or piezoelectric sensors. Similar to Coriolis flow meters, there exists a minimum flow rate below which vortices are not formed. This threshold depends directly on the density of the medium and, for hydrogen, is approximately 350–450 g/h, depending on the gas pressure [24].

6. Preparation of mixtures for experimental studies

6.1. Physicochemical properties of H_2+NH_3 mixtures at different ammonia concentrations

Combustion of hydrogen and ammonia in a two-stage system can be conducted, as mentioned above, with different proportions of the ammonia–hydrogen mixture supplied to the pre-chamber and pure hydrogen supplied to the main combustion chamber. For this reason, the physicochemical properties of the resulting mixtures are presented in Table 2.

Table 2 presents the physicochemical properties of H_2+NH_3 mixtures at ammonia concentrations of 5, 10, 20, and 50%. The calculations were performed at a temperature of 20°C and a pressure of 5 bar. The ammonia mass ratio, MR, was defined as the mass fraction of ammonia in the hydrogen–ammonia mixture:

$$\mathrm{MR} = \frac{m_{NH_3}}{m_{NH_3} + m_{H_2}} \tag{1}$$

Table 2. Physicochemical properties of the mixtures H_2 + NH_3 [18, 19]

Quantity	Unit	5% NH_3	10% NH_3	20% NH_3	50% NH_3
Density	kg/m^3	0.4318	0.4527	0.5012	0.7385
Specific heat capacity (c_p)	J/(kg·K)	$1.37\cdot10^4$	$1.31\cdot10^4$	$1.19\cdot10^4$	8209
Specific heat capacity (c_v)	J/(kg·K)	9757	9327	8468	5891
Thermal conductivity	W/(m·K)	0.1746	0.1727	0.1684	0.1492
Dynamic viscosity	Pa·s	$8.87\cdot10^{-6}$	$8.99\cdot10^{-6}$	$9.24\cdot10^{-6}$	$1.02\cdot10^{-5}$
Kinematic viscosity	m^2/s	$2.05\cdot10^{-5}$	$1.99\cdot10^{-5}$	$1.84\cdot10^{-5}$	$1.38\cdot10^{-5}$

Changes in the physical properties of the mixture are analyzed in terms of density variation as a function of ammonia concentration (Fig. 4). The results indicate that increasing the ammonia content leads to a higher mixture density; an ammonia fraction of approximately 60% results in nearly a twofold increase. This nonlinear dependence of density on the ammonia mass fraction arises from the fact that, at constant pressure and temperature, the additive quantity is the specific volume rather than density. Owing to the large differences in specific volumes and molar masses of hydrogen and ammonia, the inverse of the linear combination of specific volumes produces a nonlinear variation in density.

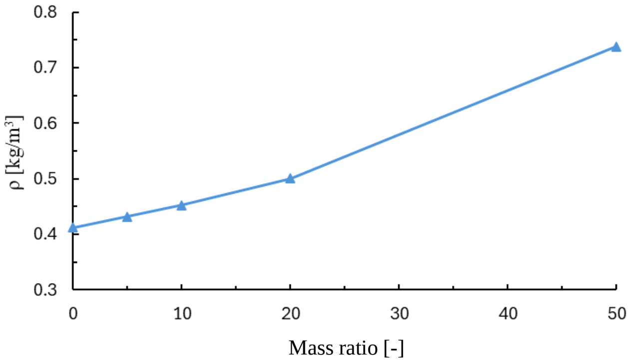

Fig. 4. Mixture density as a function of mass fraction NH_3

Changes in specific heat capacity (Fig. 5) also indicate a linear dependence on ammonia fraction. At an ammonia content of 50%, the specific heat capacity decreases by approximately 40%.

Once the NH_3 concentration exceeds approximately 20%, ammonia molecules increasingly influence the heat transfer mechanism, as they are polar species with higher molar mass and a larger number of degrees of freedom (Fig. 6).

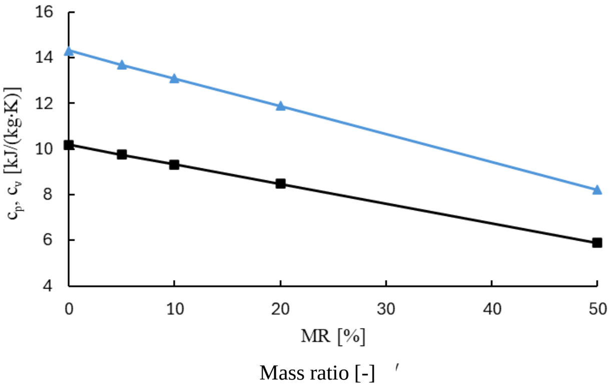

Fig. 5. Specific heat capacity at constant pressure (c_p) and at constant volume (c_v) of the mixture as a function of NH_3 mass fraction

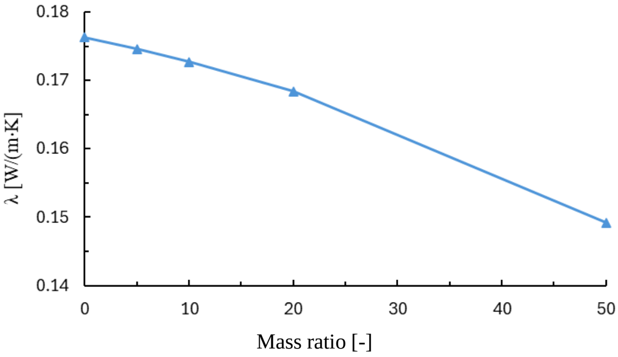

Fig. 6. Thermal conductivity of the mixture as a function of NH_3 mass fraction

Analyses of dynamic and kinematic viscosity exhibit different trends (Fig. 7). The kinematic viscosity decreases slightly, with a reduction of approximately 30% at an ammonia mass fraction of 50%. In contrast, the dynamic viscosity shows a modest increase; at a 50% ammonia content, the increase exceeds slightly 10%.

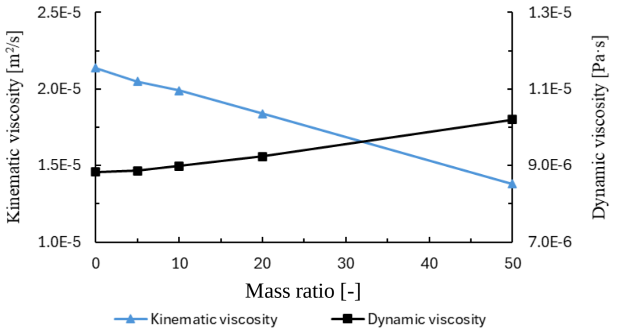

Fig. 7. Mixture viscosity as a function of NH_3 mass fraction

The degree of nonlinearity observed in the mixture properties correlates with their underlying physical mechanisms. Energy-related properties, such as c_p and c_v, are nearly directly proportional to the mass fraction, whereas geometric and transport properties, including density, viscosity, and thermal conductivity, exhibit pronounced nonlinearity.Owing to the large

Mass ratio [-]

differences between the properties of hydrogen and ammonia, even relatively small discrepancies between the assumed and actual mixture composition may lead to significant errors in flow measurement [2].

6.2. Determination of air requirement for different H_2+NH_3 mixture compositions

Air-fuel ratio (AFR) of an H_2+NH_3 mixture

Determining the air requirement in the combustion chamber of an engine fueled with a two-gas mixture, hydrogen and ammonia, requires the air-fuel ratio (AFR) of the mixture to be defined. AFR is the mass ratio of air required for complete combustion of a given mass of fuel:

$$AFR = m_{air}/m_{fuel} \tag{2}$$

For a two-gas fuel blend, the overall AFR is determined by the AFR values of the individual components and their mass fractions in the mixture. The AFR of hydrogen is 34.21:1, whereas for ammonia it is 6.06:1. Therefore, the AFR of an H_2+NH_3 mixture can be expressed as a mass-fraction-weighted average of the constant AFR values for hydrogen and ammonia.

$$AFR_{H2+NH3} = xNH_3 \cdot 6.06 + xH_2 \cdot 34.21 \tag{3}$$

where: x_{NH3} – mass fraction of ammonia, x_{H2} – mass fraction of hydrogen.

As an example, the AFR of an H_2+NH_3 mixture for an ammonia content of 10% by mass is calculated as follows:

$$AFR_{H2+NH3} = \\ 0.1 \cdot 6.06 + 0.9 \cdot 34.21 = 0.606 + 30.789 = 31.4 : 1 \tag{4}$$

The AFR value for different ammonia mass fractions in an H_2+NH_3 mixture can be represented by a linear function, whereas the FAR (Fuel–Air Ratio), defined as the inverse of AFR, follows a hyperbolic relationship (Fig. 8). The FAR curve as a function of ammonia mass fraction coincides with the excess air ratio, assuming a constant mass of air and fuel supplied to the cylinder.

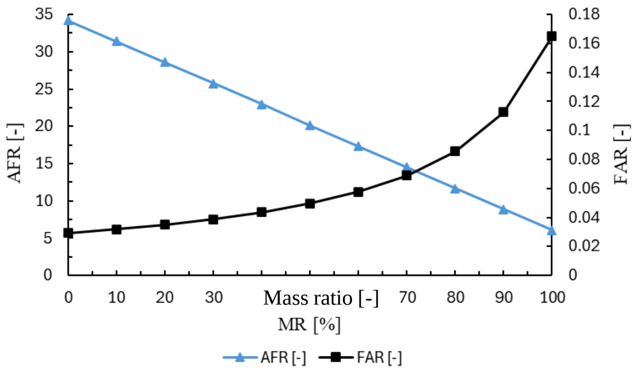

Fig. 8. AFR as a function of ammonia mass fraction (NH_3)

It is possible to convert the component concentrations of the mixture into their energy shares. Knowing the lower heating values of hydrogen and ammonia, as well as the AFR and FAR of the mixture for different compositions, the air requirement can be determined. For example, this can be expressed for different ammonia energy shares, defined as ENH_3 (ammonia energy blending ratio) – Fig. 9.

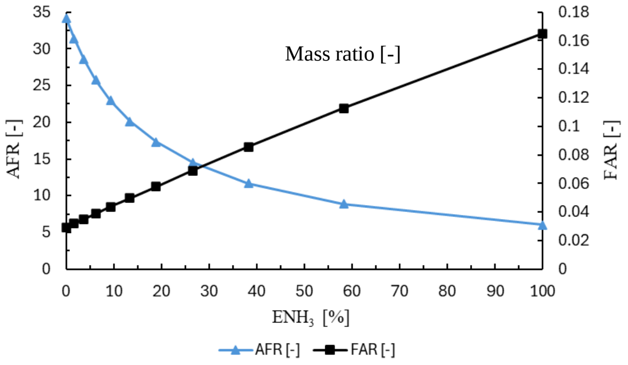

Fig. 9. AFR as a function of ammonia energy share ENH_3

Based on the relationships above, it is possible to determine the fuel dose required to produce 1 kWh of energy. Such calculations were performed for different hydrogen and ammonia concentrations (Fig. 10).

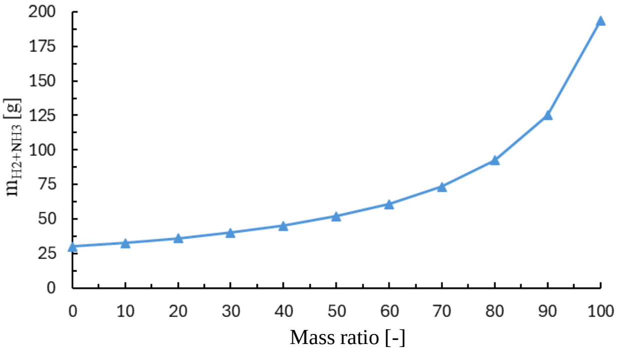

Fig. 10. Mass of the H_2+NH_3 mixture [g] required to produce 1 kWh of energy at different ammonia concentrations

Determination of the excess air ratio

Measurement of the excess air ratio plays an important role in combustion process optimization, and its value can be determined using two approaches:

- by measuring the mass flow rates of the gases supplied to the engine
- or by using an oxygen sensor (wideband lambda probe) as a control signal.

The first method for determining the excess air ratio is based on its calculation using measured mass flow rates of air and fuel supplied to the engine, with a known AFR value.

$$\lambda = m_{air}/(m_{fuel} \cdot AFR) \tag{5}$$

The second approach, based on the use of a wideband oxygen sensor, serves a control function by measuring the oxygen concentration in the exhaust gases and calculating deviations from the target excess air ratio on this basis. In addition, the detection of an excessive increase in oxygen content in the exhaust may indicate incomplete combustion or a complete lack of ignition.

Both methods are subject to measurement errors, and their results may differ slightly. This can result, for example, from an increased oxygen content in the exhaust gases when part of the fuel remains unburned and therefore is not oxidized, or from the accumulation of ammonia, which is a reducing gas, in the vicinity of the oxygen sensor.

6.3. Ammonia emissions and other exhaust components

Exhaust components of engines fueled with an H_2+NH_3 mixture

Eliminating hydrocarbons used as fuels in conventional internal combustion engines powered by hydrogen and ammonia largely excludes the formation of carbon dioxide and carbon monoxide during combustion, as well as particulate matter emissions. However, the use of hydrogen and ammonia does not eliminate the formation of other harmful species. The key concern remains the emission of nitrogen oxides (NO_x), ammonia (NH_3), and nitrous oxide (N_2O). Nitrogen oxides contribute to the formation of photochemical smog and acid rain, whereas ammonia is a toxic gas that causes irritation of the mucous membranes of the nose, throat, and eyes, and also contributes to soil and water acidification. A particularly harmful compound not commonly encountered on a large scale in conventional internal combustion engines is N_2O, whose global warming potential is approximately 300 times higher than that of CO_2 over a 100-year time horizon, and which also contributes to ozone layer depletion.

Expected concentration ranges of NH_3, NO_x, and N_2O in exhaust gases

Based on experimental studies, including [15], it is possible to predict the concentrations of NH_3, NO_x, and N_2O formed during the combustion of an H_2+NH_3 mixture as a function of its composition. In the referenced study, a four-cylinder spark-ignition engine was used, fueled with hydrogen via the original direct injection system and with ammonia supplied through port fuel injection into the intake manifold. During the experiments, constant operating conditions were maintained ($n = 1500$ rpm, $M_o = 40$ Nm). Measurements were conducted at two different excess air ratios, $\lambda = 1$ and $\lambda = 1.2$ (Fig. 11).

For different ammonia concentrations in the mixture, the ignition timing was adjusted to MBT (Maximum Brake Torque) under stoichiometric conditions. Subsequently, the influence of ammonia concentration on emissions at $\lambda = 1.2$ was evaluated using a different ignition timing, adjusted to MBT for lean operation, which is presented in the subsequent plots as $\lambda = 1.2$/MBT.

Initially, as the ammonia mass fraction increased, the concentration of ammonia in the exhaust gases rose gradually. When the ammonia share exceeded approximately 80%, the amount of unburned ammonia increased sharply, which is also reflected in an increase in specific fuel consumption at high NH_3 concentrations. Differences in unburned ammonia emissions between $\lambda = 1$ and $\lambda = 1.2$ remain small over most of the composition range; only at low hydrogen content does the NH_3 concentration become noticeably lower when operating with a lean mixture (Fig. 11).

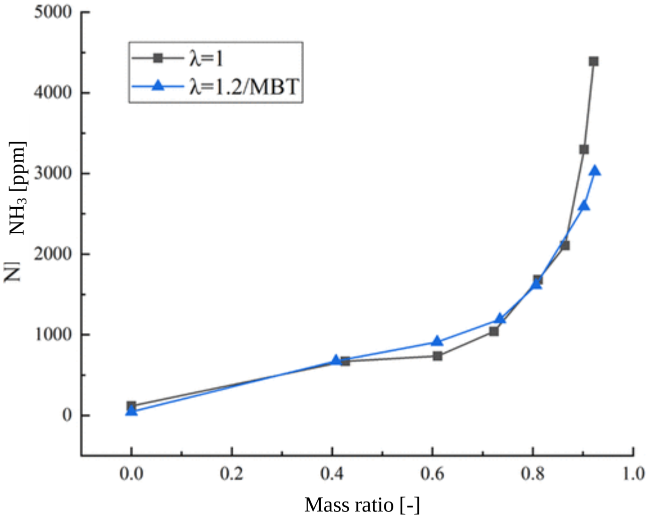

Fig. 11. NH_3 concentration in exhaust gases as a function of NH_3 mass fraction in the mixture [15]

The variation in NO_x concentration in the exhaust gases followed a markedly different trend. When the engine was fueled with hydrogen, nitrogen oxides were formed primarily through oxidation of atmospheric nitrogen in the intake air (Fig. 12). For an H_2+NH_3 mixture with an ammonia mass fraction of MR = 0.4, corresponding to an ammonia energy share of approximately 10%, a sharp increase in NO_x concentration was observed, particularly at $\lambda = 1.2$. Further increases in the ammonia fraction in the mixture resulted in a reduction of NO_x concentration (Fig. 13). This trend is mainly attributed to the contribution of fuel-bound nitrogen to NO formation, described by the NO_{fuel} mechanism.

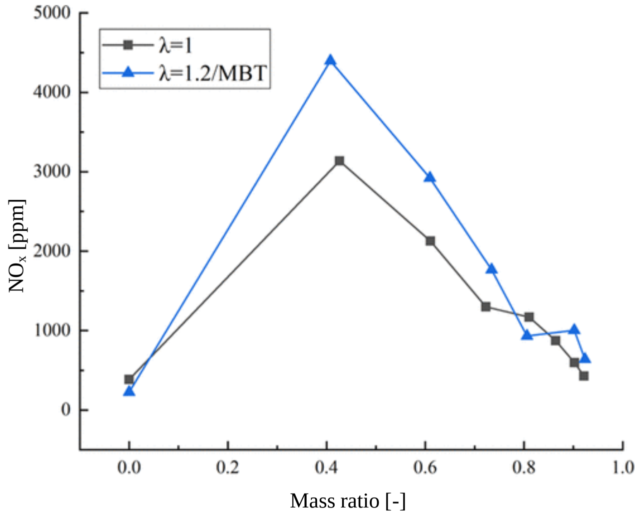

Fig. 12. NO_x concentration in exhaust gases as a function of NH_3 mass fraction in the mixture [15]

During combustion of an H_2+NH_3 mixture, nitrous oxide (N_2O) is formed mainly via the reaction $NH + NO \rightarrow N_2O + H$, which proceeds particularly intensively under conditions of high pressure and low temperature (Fig. 13). Under high-temperature conditions, N_2O reacts with hydrogen, forming N_2. Consequently, as the ammonia mass fraction increases, the combustion temperature decreases and the concentration of hydrogen radicals is reduced. These factors promote N_2O formation while simultaneously inhibiting its decomposition, leading to a gradual increase in N_2O concentration in the exhaust gases.

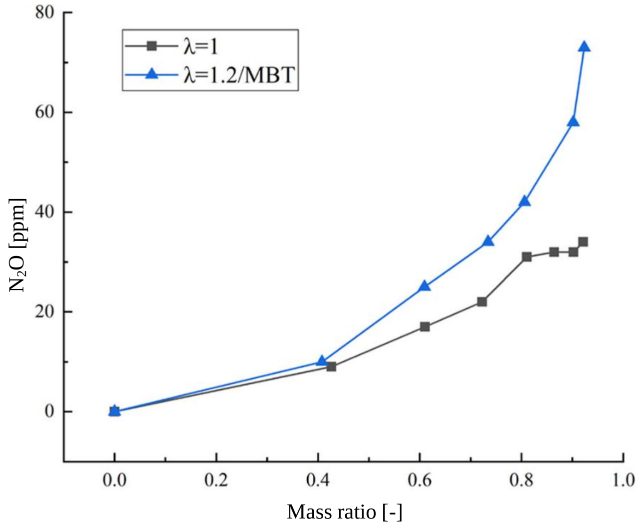

Fig. 13. N_2O concentration in exhaust gases as a function of NH_3 mass fraction in the mixture [15]

In summary, increasing the ammonia fraction in the fuel leads to a significant rise in N_2O and unburned NH_3 concentrations. At an ammonia mass fraction of approximately 40%, the concentrations of N_2O and NH_3 in the exhaust gases remain relatively low, whereas the NO_x concentration is very high, in the range of 3000–4500 ppm. This behavior is attributed to the formation of so-called fuel-NO_x, generated through reactions between atomic nitrogen as well as NH and NH_2 radicals with oxygen. In the studies analyzed above, measurements were not performed for lower NH_3 fractions. Therefore, it cannot be determined how NO_x concentrations would vary at ammonia mass fractions of 10%, 20%, or 30%.

In the studies described above, the excess air ratio was set to $\lambda = 1$ or $\lambda = 1.2$. However, TJI engines are capable of operating with lean mixtures at excess air ratios of $\lambda = 2$ or higher. In the study by Huo et al. [11], the effects of hydrogen fraction and excess air ratio on the combustion process of an H_2+NH_3 mixture in a marine engine equipped with a pre-chamber were analyzed using CFD (computational fluid dynamics) simulations (Fig. 14).

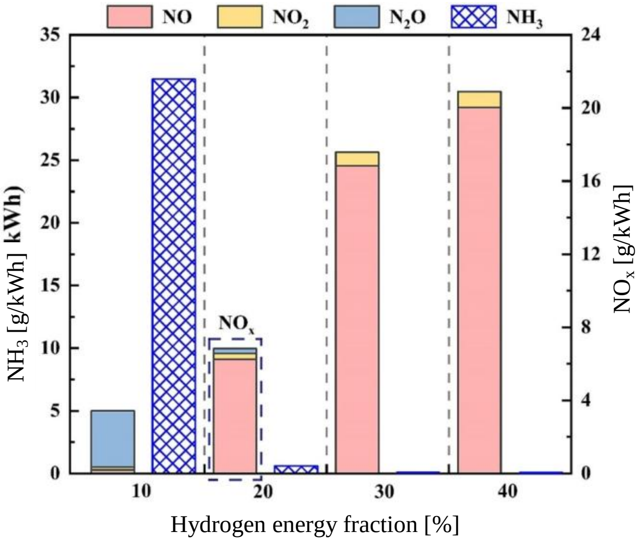

Fig. 14. NH_3 and NO_x emissions at different hydrogen energy fractions [11]

The primary harmful species emitted by engines fueled with a hydrogen–ammonia mixture are NO_x and unburned ammonia. The influence of hydrogen energy share on the emissions of these compounds is presented above. At a hydrogen energy share of 10%, corresponding to a hydrogen mass fraction of 1.69%, unburned ammonia emissions are high and reach 31.5 g/kWh. This is caused by a flame front with insufficient temperature and low propagation speed. Increasing the hydrogen energy share to 20% results in an almost complete elimination of NH_3 emissions and a significant reduction in N_2O emissions. However, the associated increase in flame front temperature promotes the formation of high-temperature NO and NO_2.

Figure 15 compares NO_x and NH_3 concentrations at different equivalence ratios (ϕ). At very lean conditions (ϕ = 0.4, corresponding to λ = 2.5), the highest unburned ammonia emissions were observed, which is also associated with an increased N_2O concentration in the exhaust gases. The low combustion temperature under these conditions promotes incomplete combustion and favors the formation of nitrous oxide. Increasing the equivalence ratio improves mixture reactivity, leading to reduced NH_3 and N_2O emissions, but at the same time contributes significantly to higher emissions of NO and NO_2.

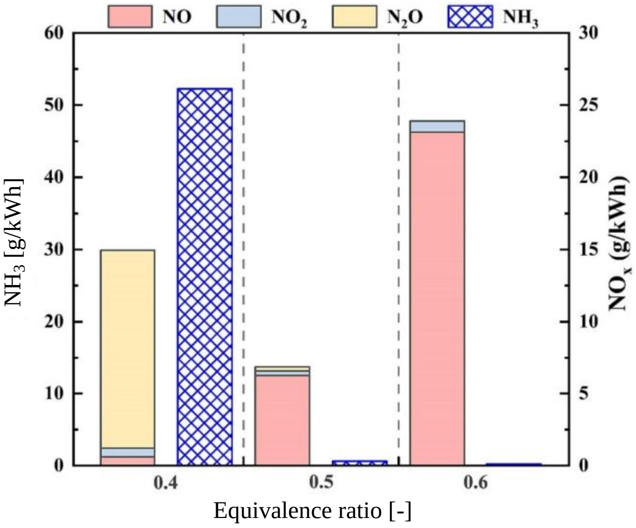

Fig. 15. NH_3 and NO_x emissions with different equivalence ratios [11]

Taking into account the presented experimental studies and simulations, general conclusions can be drawn regarding the influence of H_2+NH_3 mixture composition and excess air ratio on nitrogen compound emissions from engines fueled with hydrogen and ammonia. NO_x formation occurs either at high temperatures in the range of 1100–1400°C through thermal-NO_x mechanisms, or via oxidation reactions involving fuel-bound atomic nitrogen and NH and NH_2 radicals originating from ammonia decomposition, referred to as fuel-NO_x.

Increasing the hydrogen concentration in the mixture raises the flame front temperature and consequently leads to higher emissions of nitrogen oxides formed at high temperatures (thermal-NO_x). Conversely, at very low hydrogen content or at high excess air ratios (λ), the flame front may exhibit insufficient temperature and propagation speed, resulting in increased emissions of ammonia and its radicals and, consequently, enhanced formation of fuel-NO_x.

In addition, for certain H_2+NH_3 mixture compositions, both thermal-NO_x and fuel-NO_x formation pathways may occur simultaneously, which can result in particularly high emissions of these exhaust species [11].

Summary

Efforts to reduce emissions generated by the combustion of fossil fuels are driving the search for effective alternatives in the form of carbon-free compounds such as hydrogen and ammonia.

The properties of these compounds discussed in the article, including their combustion characteristics and expected emission ranges, indicate their potential as promising future fuels. Particular attention is given to the use of an H_2+NH_3 mixture, which is justified through analysis of storage options, mixture formation methods, combustion behavior, and resulting emissions.

Efficient combustion of hydrogen and ammonia can be achieved using a two-stage combustion engine based on the Turbulent Jet Ignition (TJI) concept, which addresses many of the limitations of conventional spark-ignition engines.

Measurement of the mass flow rates of the considered fuels is challenging due to the physicochemical properties of hydrogen and ammonia, and especially due to the large differences between them. Nevertheless, solutions currently exist that enable precise measurement of H_2+NH_3 mixture flow rates. The operating principles, advantages, and limitations of these measurement methods are discussed in the article.

Nomenclature

AFR	air-fuel ratio
AFT	adiabatic flame temperature
CFD	computational fluid dynamics
E	energy
ENH_3	ammonia energy blending ratio
HoC	heat of combustion
IDT	ignition delay time
LFS	laminar flame speed
MBT	maximum brake torque
MIE	minimum ignition energy
MR	mass ratio
NH_3	ammonia
TJI	turbulent jet ignition
λ	air excess ratio
ϕ	equivalence ratio

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