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Potential of water addition in ammonia spark ignition engines

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Abstract

The use of carbon-free fuel like the hydrogen and its derivate, ammonia, is more and more considered for different applications, even for the transportation sector to reduce CO₂ emissions. As ammonia is considered as the hydrogen carrier, it can be also considered as a fuel. However, not only ammonia is toxic and corrosive due to its alkaline properties, but also its narrow flammability limits, high auto-ignition temperature and low flame velocity are the challenges to overcome for NH₃ fueled in internal combustion engine. The combustion instabilities at low loads and / or high engine speed and unburnt NH₃, NO_x and N₂O emissions minimization are the key points to make NH₃ a potential fuel candidate for premixed combustion engines. To guarantee the performances and the stability of the engine, H₂ is often considered as a combustion promoter. Water injection is one mean to decrease thermal NO_x emissions in current Spark Ignition engine. But only a few studies provide some results to evaluate this potential strategy for ammonia combustion as NO_x is also formed by fuel-NO_x road. The objective of this study is to experimentally explore the water addition in SI engine at compression ratio of 14. The experimental results addressed the combustion behavior with the exhaust gases emissions (NO_x, and NH₃) in the case of water addition of using pure NH₃ blended or not with hydrogen at 1000 rpm. Kinetics simulations will help for providing some analysis.

Introduction

Due to its unfavorable characteristics of combustion, a combustion promoter has to be considered to run current SI engine, i.e. regular compression ratio and igniter, with NH₃ as fuel especially when no boosted conditions are considered, i.e. in medium and low load as summarized in [1]. To consider ammonia engine as a reality, combustion ignition and stabilities and engine performances have to be enhanced, as example by blending with hydrogen. But it is necessary to state about a trade-off between exhaust emissions of NO_x and unburnt NH₃ [1-3]. The formation of NO_x in NH₃-air and NH₃-H₂-air combustion includes both thermal and fuel NO_x. Liquid or steam water injection is more and more considered for thermal engines. Indeed, it can provide a heat sink that lowers the flame temperature and reduces thermal NO_x formation. Thankfully, the amount of water injected is so minimal that the piston stroke is not affected in any feasible way by the fluid. Water Injection and cooled exhaust gas recirculation (EGR) could be seen as competitive technologies: it has been demonstrated that at medium load in Diesel engine, a 40-50 % Water-to-Fuel Ratio has the same effect as an EGR-rate of 10%, which is seen as relatively low even for thermal engines [4, 5]. The objective of water injection is to affect the kinetic chemistry. Indeed, the 'DeNO_x' process can be promoted reducing the NO_x emission and as chemical collider steam water can decrease the NO formation. In [6] an interesting comparison is done between the effect of ammonia or water injection in a diesel engine. The idea of ammonia solution (NH₃ + H₂O) was also investigated in a Diesel Compression Ignition engine [7-9]. A decrease of NO_x emissions due to the lower combustion temperature was obtained but with an

increase of the unburnt hydrocarbon [7] while in [9], the opposite trends were obtained (HC and CO decreasing trends as NO_x increased with the increase of the equivalence ratio). But, up to date, no experimental studies have been carried out on the NO_x reduction potential by water addition on ammonia/hydrogen Spark-Ignition engine.

The objective of this study is to evaluate the possibility and the potential of water vapor addition by running a single cylinder spark-ignition engine (Compression Ratio 14) fed with 3 different ammonia/hydrogen blends (10, 20, 30% of H₂) for different equivalence ratio from lean to rich conditions (from 0.7 to 1.2), by replacing 8.5% of fuel blend by water vapor at the 1000 rpm. In addition, to support and better understand the findings, simulations were conducted with a zero-dimensional, two-zone Spark Ignition engine model based on the NH₃ reaction mechanism of Stagni *et al* [10], to highlight some tendencies of exhaust gases such as NO, NO₂, N₂O.

Experimental set-up

The engine experiments were conducted in a single-cylinder long-stroke spark-ignition engine (based on PSA-EP6) with a flat piston and a pent-roof chamber. The engine specifications are indicated in Table 1. More information can be found in [11]. The engine is driven by an electric motor maintained at 1000 RPM. The main shaft is equipped with a Kubler optical encoder for angular position monitoring with a 0.1 Crank Angle Degree (CAD) resolution. The Intake valve closure is -180 CAD bTDC and the exhaust valve opening is 150 CAD aTDC.

Table 1: Engine Characteristics

Displaced volume	0.535 L
Stroke	115 mm
Bore	77 mm
Connecting rod length	177 mm
Compression ratio	14
Number of valves	4
Coolant and oil temperature	80 °C
Regime	1000 rpm
Pin, Tin	1 atm., 55°C

The spark plug used is the original one with a coil charging time set to 2 ms (~80mJ). The gaseous flows are preheated to the intake temperature were measured and controlled using Brooks thermal mass flowmeters with +/- 0.7% accuracy. The water content is controlled using a Brooks Coriolis flowmeter before passing through a heater and is blended with air/fuel inside the plenum volume.

The wet exhaust gases were analysed using a Gasetm Fourier Transform Infrared (FTIR) spectrometer to assess NO, N₂O and NH₃ concentrations.

A water-cooled AVL piezoelectric pressure transducer with a 0.1 CAD resolution provides in-cylinder pressure measurements. Its measuring range is 0–25 MPa. Engine intake and exhaust temperature and pressure are monitored using type K thermocouples and piezo-resistive absolute pressure transducers. The absolute cylinder pressure is obtained by equalizing the in-cylinder pressure and the mean absolute intake pressure (Pin), 20 CAD in the middle of the intake stroke. The apparent Heat Release Rate (aHRR) was computed from pressure trace post-processing with the first law of thermodynamics, as follows:

$$aHRR = \frac{daHR}{d\theta} = \frac{\gamma}{\gamma - 1} \cdot P \cdot \frac{dV_{Cyl}}{d\theta} + \frac{1}{\gamma - 1} \cdot P \cdot \frac{dP_{Cyl}}{d\theta}$$

where is the heat γ capacity ratio, $PCyl$, $VCyl$ and θ , the cylinder pressure, volume, and crank angle respectively. The Burnt Mass Fraction (BMF) is obtained by integrating the heat release using a constant γ . Then the apparent aHRR is recalculated using the variable heat capacity ratio γ computed from the previous BMF.

At each operating condition, an optimum Start Ignition Time was selected to guarantee, when it is possible, a minimum Coefficient of Variation of IMEP (COV_{IMEP}) defined as the standard deviation of IMEP on the mean IMEP.

0D Simulations

Kinetic calculations were performed using two-zone SI engine model in Chemkin Pro (ANSYS) in order to enhance the chemical process. The spark ignition timing and the experimental crank-angle degrees where 10%, 50%, and 90% of BMF are reached are the input data to fit the Wiebe function for the built-in 0D simulation. This function describes the mass transfer between the 2 zones. Classical Woshni coefficients have been chosen to estimate the heat losses in the simulation. The kinetic mechanism used is from Stagni

et al. [10] made of 31 species and 203 reactions. This model is one of the best accurate to predict any chemical heat release and to highlight some tendencies of exhaust gases such as NO_x, and N₂O and unburnt emissions [12].

Conditions

The performances and the pollutants emissions are compared for 3 different ammonia/hydrogen blends (10, 20, 30% of H₂) for a range of equivalence ratio (ER, defined with N₂ and H₂O as products) from lean to rich conditions (from 0.7 to 1.2). For this first study, a vapor water injection amount of 8.5% substituted in the fuel has been considered. The intake air quantity was adjusted to keep constant the equivalence ratio. It has to be mentioned that it was not possible to get the stability criteria for NH₃ fuel only with water addition, even if the water amount is very small for this study. It needs the help of hydrogen to stabilize the engine by at least 10% content in the fuel. The replacement of 8.5% of total fuel by water induces a small change in the Lower Heating Value (LHV) with a maximum of 2% as highlighted in Table 2 where the difference in LHV ('Input column'), in %, relative to the cases without water addition is given for all conditions.

Table 2: Difference (in %) in Energy Input (Reaction Heat) and in Energy Output (IMEP) relative to the case without water addition.

ER	10% H ₂		20% H ₂		30% H ₂	
	Input	Output	Input	Output	Input	Output
0.7	-1.41	-53.33	-1.45	-16.67	-1.50	-9.68
0.8	-1.57	-20.59	-1.62	-19.40	-1.67	-11.59
0.9	-1.73	-11.11	-1.78	-11.11	-1.83	-12.00
1	-1.87	-12.66	-1.92	-11.39	-1.98	-11.11
1.1	-2.01	-12.20	-2.07	-13.41	-2.12	-12.20

Results

As it can be seen in Figure 1, as the amount of water is in the fuel blend, the effect of decrease input energy decreases the IMEP even if there is no cooling as it is in gaseous water, especially for lowest H₂ content and equivalence ratio below 0.85.

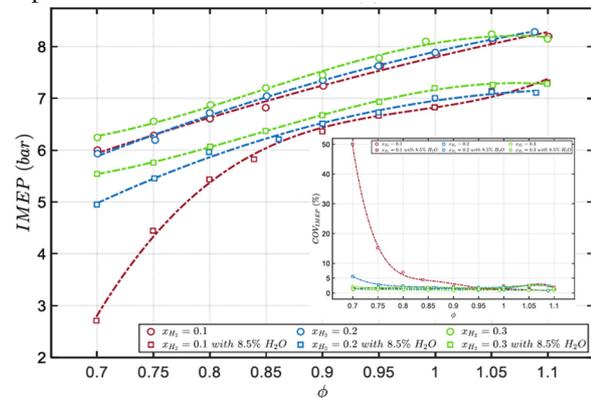


Figure 1: Effect of water injection on IMEP as a function of the equivalence ratio (ϕ) for 3 NH₃/H₂ blends.

Therefore, the replacement of fuel by 8.5% of water affects more combustion stability and performance than

only 2% of LHV. This can be seen in Table 2, as except for 90NH₃/10H₂ (10%H₂) in the leanest conditions ($\phi=0.7$), the relative difference in IMEP ('Output') is around 11-12% when the engine is stable, i.e. COV_{IMEP} below 5%.

The combustion duration, determined at the Crank-Angle degree difference from 90% of BMF and 10% BMF, is plotted in Figure 2. As expected, the increase of the equivalence ratio increases the combustion development and the combustion velocity is enhanced by the replacement of ammonia by hydrogen as highlighted in [9]. The water addition slows down the combustion. An average of 4 CAD of combustion increase obtained with water does not seem to be affected by H₂ content, except for the case 90NH₃/10H₂ for leaner mixture (below 0.85). It is interesting to notice also that identical combustion duration was obtained between 70NH₃/30H₂ (30% H₂) with water and 90NH₃/10H₂ without water.

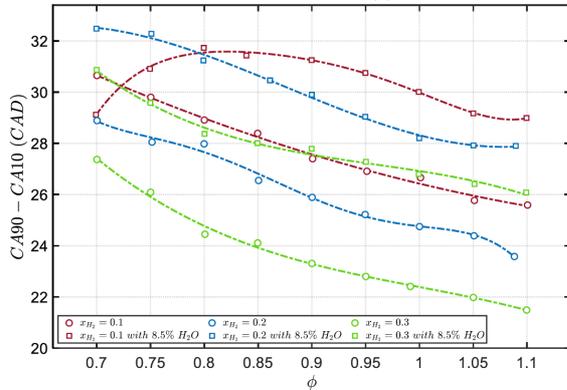


Figure 2: Effect of water injection on combustion duration as a function of the equivalence ratio for 3 NH₃/H₂ blends.

Exhaust emissions

As the addition of hydrogen improves the combustion of ammonia, the emissions of unburnt ammonia are strongly reduced as it can be seen in Figure 3, even if the minimum level remains important (2800 ppm). As the water does not facilitate the ammonia combustion, the unburnt NH₃ emissions are increased by a factor 1.5, but remains under 1% for 30 and 20% of H₂ in the blend.

A combustion efficiency can be estimated based on unburnt NH₃ emissions, even if unburnt H₂ emissions were not measured for this study, to evaluate the effect on ammonia combustion. Figure 4 proves that the best efficiency in terms of combustion is obtained for mixtures near the stoichiometry (0.95 to 1.05).

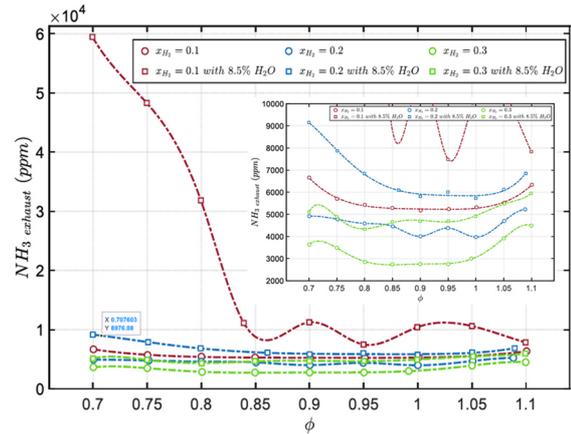


Figure 3: Effect of water injection on the unburnt ammonia exhaust as a function of the equivalence ratio for 3 NH₃/H₂ blends.

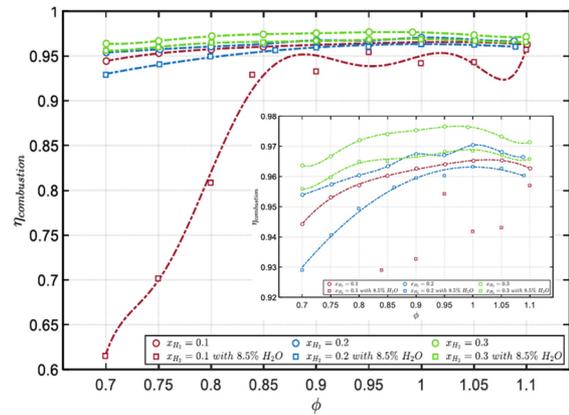


Figure 4: Effect of water injection on the combustion efficiency as a function of the equivalence ratio for 3 NH₃/H₂ blends.

By considering NO_x emissions in Figure 5, the addition of H₂ in the fuel induces an increase of NO_x at ER>0.9 but a decrease of NO_x at ER<0.9. However, it is clear that the addition of water, even in small amounts can decrease NO_x emissions as here by more than 45% in lean mixtures as found previously with 8% of N₂ dilution [10]. The impact is found reduced but still significant when operating conditions around the stoichiometry are considered, between 0.95 to 1.05 of equivalence ratio. More details are given in the following section. About N₂O emissions (Figure 6), no clear tendencies as a function of the equivalence ratio, the H₂ content or the water addition can be drawn: except for lowest H₂ mixture, all values are below 50 ppm, no far from the limit of measurement accuracy. The lowest emissions can be found for mixtures around stoichiometry (1 – 1.05).

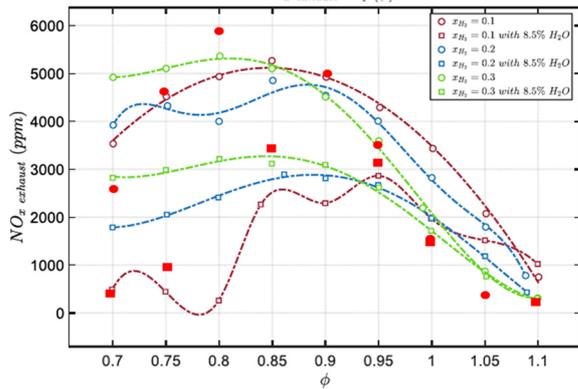


Figure 5: Effect of water injection on NOx emissions as a function of the equivalence ratio for 3 NH₃/H₂ blends. Red filled symbols obtained from simulation for x_{H2}=0.1.

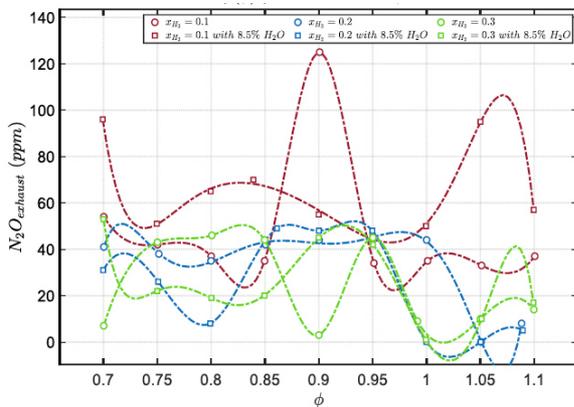


Figure 6: Effect of water injection on N₂O emissions as a function of the equivalence ratio for 3 NH₃/H₂ blends.

Simulated results

The simulated averaged NO mole fractions are added in Figure 5, compared to the experimental measurements performed at the exhaust of the engine, for 90NH₃/10H₂ blend. The comparison indicates a global good agreement with the experimental measurements. This confirms that the H₂O substitution does not affect the simulated NOx emissions for an ER comprised between 0.9 and 1.1.

Figure 7 represents the variation of average p and T as function of CAD for four operating conditions, with and without water and ER equal to 0.75 and 0.95. In presence of water compare to neat mixture, the decrease of the maximum of T is around 160 K at both ER but the maximum of p decreases by 23 atm and 10 atm, respectively at ER equal to 0.75 and 0.95. The averaged NO species profiles increase during the temperature increase. Due the high temperature range ($T > 2100$ K), NO is mostly formed through the well-known thermal-NO route. The fuel-NO route ($\text{NH}_3 > \text{NH}_2 > \text{NH} > \text{HNO} > \text{NO}$) is more efficient at ER=0.75 due the highest OH quantities than at ER=0.95.

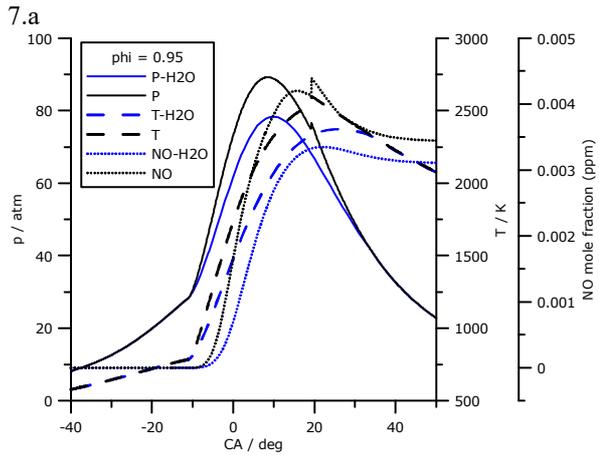
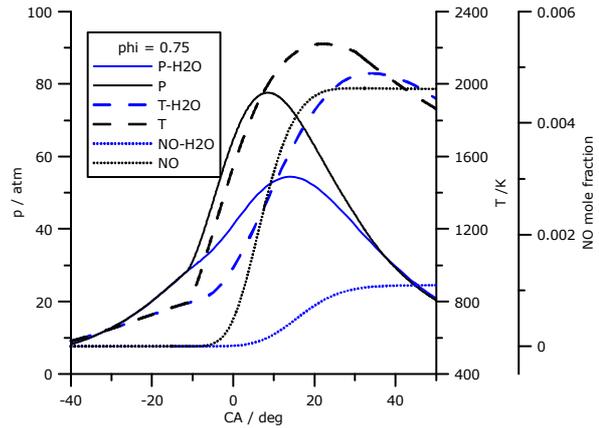


Figure 7. Simulated in-cylinder pressure and Temperature as function of CAD at ER equal to a/ 0.75 and b/ 0.95.

The analysis of the rate-of-progress (ROP) of NOx has been performed in case of ER=0.95 and 0.75 with and without water in order to better highlight the water effects. The ROP analysis of NO (Figure 8a) indicates that without H₂O, NO species are consumed and then formed at both ER (black curves). In presence of H₂O (blue curves), NO species are also first consumed and second formed at ER= 0.95, but at ER=0.75 NO species are only slightly consumed. Examination of the individual reaction ROP shows that reaction $\text{OH} + \text{NO} \rightleftharpoons \text{HONO}$ follow similar tendencies as those of the Total NO in the 4 studied cases (Figure 8b). The total OH-ROP analysis indicate that OH radicals are consumed during all the cycle. But, the OH-ROP due to reaction $\text{H}_2\text{O}_2(+\text{M}) \rightleftharpoons 2\text{OH}(+\text{M})$ follows also the similar tendencies (Figure 8c) with a specific consumption of OH at ER=0.75 in presence of H₂O. This reaction is not only pressure-dependent but also third-body efficient dependent. Water substitution not only affects the in-cylinder pressure and temperature but also the formation of OH. OH radicals are the main oxidizer of NH₃ and H₂ which turn to modify the NO formation.

Further analysis is necessary to discriminate the effect of pressure, temperature and chemistry on the decreasing of NO at the exhaust of the engine.

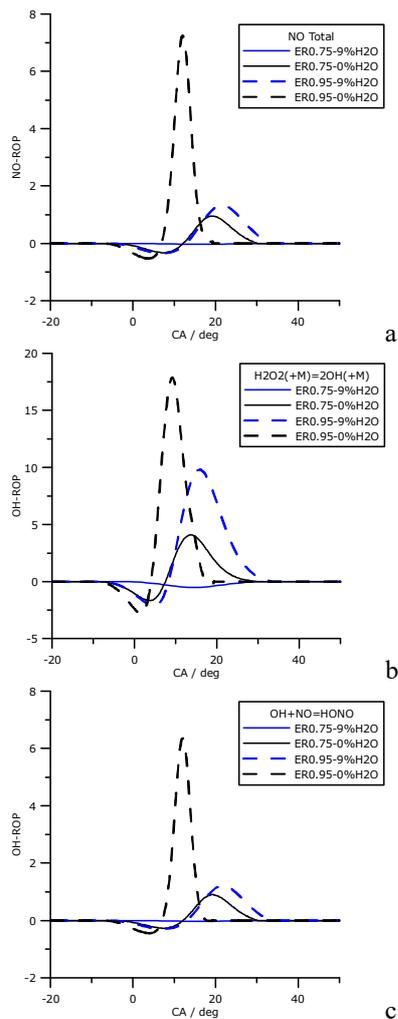


Figure 8. Rate-of-Progress (ROP) of a/ Total NO and OH through reactions b/ $\text{H}_2\text{O}_2(+\text{M}) \rightleftharpoons 2\text{OH}(+\text{M})$ and c/ $\text{OH}+\text{NO} \rightleftharpoons \text{HONO}$.

Conclusion

First results are provided in this experimental study about the potential of water addition in NH_3/H_2 fuel to reduce NO_x emissions as is considered for hydrogen thermal engine. The small quantity of water injected (8.5% in vol. of the fuel), which only represents a maximum decrease of 2% in LHV, induces engine instability requiring more hydrogen amount in the blend to ensure stability and lower unburnt ammonia emissions. In the case of lean NH_3/H_2 mixture, it can be concluded that NO_x is strongly reduced by water presence, even if both thermal and fuel NO_x routes are involved. This is due to the change of OH radicals, pointed out by the simulated by OD 2 zone model. It is pointed out that further analysis and studies are necessary to discriminate the effect of in-cylinder pressure and temperature and chemistry on the decreasing of NO at the exhaust of the engine.

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