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Experimental investigation of nitrogen based emissions from an ammonia fueled SI-engine

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HIGHLIGHTS

- An experimental comparison of emissions from gasoline and ammonia fueled SI-engine.
- Investigation of mechanisms governing the emissions of nitrogen based emissions.
- Proposed mechanism for unburned NH_3 in NH_3/H_2 fueled SI-engine.
- Application of SCR catalyst for exhaust after-treatment is evaluated.

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ABSTRACT

This study concerns nitrogen based emissions from a hydrogen enriched ammonia fueled SI engine. These emissions deserve special attention as their formation may differ from conventional HC combustion due to the nitrogen content in the fuel. A range of experiments are conducted with a single cylinder 0.612 l CFR engine with a compression ratio varying from 7 to 15 using a fuel composition of 80 vol% NH_3 and 20 vol% H_2. Wet exhaust samples are analysed with an FT-IR. Emission measurements reveal that nitric oxide stem from other reaction paths than the dissociation of molecular nitrogen. This causes the NO emissions to peak around 35% rather than 10% excess air, as is typical in HC fueled SI-engines. However the magnitude of NO emissions are comparable to that of measurements conducted with gasoline due to lower flame temperatures. Nitrogen dioxide levels are higher when comparing with gasoline, but has a relatively low share of the total NO_x emissions (3–4%). Nitrous oxide is a product of NH_2 reacting with NO_2 and NH reacting with NO. The magnitude is largely affected by ignition timing due to the temperature development during expansion and the amount of excess air, as increased oxygen availability stimulates the formation of the NH_2 radical and the levels of NO_2 are higher. Under ideal operating conditions (MBT ignition timing) N_2O levels are very low. The dominating contributors to unburned ammonia are chamber crevices as the magnitude of these emissions is greatly affected by the compression ratio. However, levels are lower than required in order to eliminate all NO_x emissions with a SCR catalyst.

1. Introduction

The present work is a further study of ammonia/hydrogen as fuel in an SI-engine. The idea of use of ammonia as fuel for an IC engine can be traced as far back as 1905. The first application of this fuel was in Belgium in 1942 where it was suggested as an alternative to diesel oil in buses [1]. The fuel used in these buses was composed of ammonia vapour and coal gas. Later investigations concerning fuel composition reveal that a hydrogen content of 2–3% mass will promote the combustion of ammonia sufficiently to achieve satisfactory engine performance in an SI-engine [2]. The hydrogen was dissociated from the ammonia via catalytic reactions driven by the engine exhaust heat. A similar fuel system was proposed in investigations conducted prior to the current work, where the use of a metal amine complex was proposed to achieve a feasible energy density and safe storage of the fuel [3]. These investigations similarly reveal that a fuel mixture consisting of 10–20 vol.% H_2 display favourable combustion characteristics for a SI-engine, and that the exhaust heat can be used to effectively desorb the ammonia from the metal amine complex. Other traits of the fuel are its lack of carbon, omitting soot- and carbon oxide emissions. Investigations of the CO_2 abatement potential in vehicles shows that an ammonia fueled SI-engine is a strong alternative to BEV‘s and FCEV‘s with regard to CO_2 abatement cost [4]. One of the concerns for using this fuel in vehicles are the nitrogen based emissions. Nitrogen oxides such as NO and NO_2 participate in ozone layer depletion, cause respiratory problems and may be fatal under prolonged exposure. When mixed with air in the atmosphere NO may convert to nitric acid which leads to acid rain

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Table 1
Range of engine operation modes.

Fuel type	Gasoline RON 98	0.8 NH_3 0.2H_2
CR (–)	7	7–15
λ (–)	1–1.3	1–1.4
Ignition timing (°BTDC)	0–30	0–40
Throttle	Fully open	Fully open
Speed (rpm)	1000	1000

and NO_2 is responsible for smog in and around urban areas. N_2O is a major concern due to its high global warming potential around 300 times that of CO_2 over a time horizon of 100 years. In addition, the fuel itself is toxic and the amount of unburned fuel in the exhaust may be problematic for vehicles. The current work concerns the impact of using a fuel with a high nitrogen content on the emissions of nitrogen oxides and the concern of toxic unburned fuel. The levels of these emissions are measured under various parameters and compared to conventional gasoline emissions from the same engine under same parameter sweeps. The engine operation modes are specified in Table 1. This comparison will distinguish formation patterns of nitrogen oxides and unburned fuel from that of conventional gasoline, and identify the mechanisms at work.

2. Engine out emissions

2.1. Formation of nitrogen oxides

It is well known that the emission of nitric oxide is present under combustion and high temperature processes. It is formed from oxidation of dissociated atmospheric nitrogen at high temperatures, >1800 K. This process is well predicted by the Zeldovich chemical kinetic mechanism [5,7]. The governing parameters of this mechanism is time, temperature and oxygen availability. The Zeldovich reactions are expressed in Table 2.

Sources of nitrogen, other than atmospheric N_2, may also contribute to the formation of nitric oxide. It will however follow a different reaction path. The theory behind these reaction pathways are limited and not as well established as the Zeldovich mechanism. DeSoete proposed a global kinetic mechanism for the formation of nitric oxide from oxidation of nitrogen containing species (NH_3 and HCN) [10].

The formation of nitric oxide from HCN is also known as prompt NO and is not present in the combustion of ammonia due to the absence of carbon. DeSoete's mechanism suggests a reaction order for oxygen in Reaction (1) in Table 3 related to the excess of air. This mechanism predicts faster NO formation than the Zeldovich mechanism depending on the oxygen availability, Eq. (1), causing the formation of NO to be significant at temperatures much lower than 1800 K, Fig. 1.

$$b = \begin{cases} 1 & X_{O_2} \leqslant 0.0041 \\ -3.95 - 0.9\ln X_{O_2} & 0.0041 \leqslant X_{O_2} \leqslant 0.0111 \\ -0.35 - 0.1\ln X_{O_2} & 0.0111 < X_{O_2} < 0.03 \\ 0 & X_{O_2} \geqslant 0.03 \end{cases} \tag{1}$$

Table 2
Zeldovich reaction mechanism for NO formation from dissociated N_2 with concentration in $\left[\frac{mol}{m^3}\right]$.

	Reaction	Reaction rate $\left[\frac{m^3}{mol\cdot sec}\right]$
1f.	$O + N_2 \rightarrow N + NO$	$1.8 \cdot 10^8 \cdot \exp\left(\frac{-38370}{T}\right)$
1r.	$N + NO \rightarrow O + N_2$	$3.8 \times 10^7 \cdot \exp\left(\frac{-425}{T}\right)$
2f.	$N + O_2 \rightarrow O + NO$	$1.8 \times 10^4 \cdot T \cdot \exp\left(\frac{-4680}{T}\right)$
2r.	$O + NO \rightarrow N + O_2$	$3.81 \times 10^3 \cdot T \exp\left(\frac{-20820}{T}\right)$

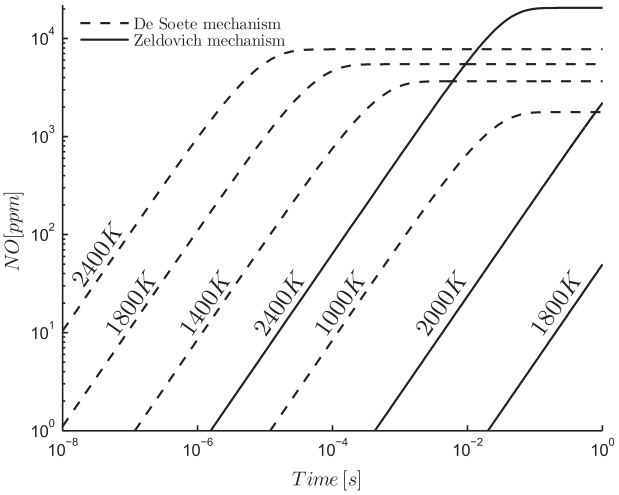

Fig. 1. Formation of NO at various temperatures from one mol air according to the Zeldovich mechanism and stoichiometric oxidation of one mole of ammonia according to the De Soete mechanism.

Table 3
DeSoete mechanism for formation of NO from oxidation of NH_3 with concentration in mol fraction.

	Reaction	Reaction rate (s^{-1})
1.	$NH_3 + O_2 \rightarrow NO + H_2O + \frac{1}{2}H_2$	$4 \times 10^6 \exp\left(\frac{-16114}{T}\right)$
2.	$NH_3 + NO \rightarrow N_2 + H_2O + \frac{1}{2}H_2$	$1.8 \times 10^6 \exp\left(\frac{-13596}{T}\right)$

Experimental investigations reveal that nitrogen dioxide forms rapidly in the flame zone from nitric oxide through proposed Reaction (2).

$$NO + HO_2 \rightarrow NO_2 + OH \tag{2}$$

Subsequently NO_2 is converted back to NO in the post flame region via proposed Reaction (3) [11].

$$NO_2 + O \rightarrow NO + O_2 \tag{3}$$

An explanation for the appearance of NO_2 in combustion products from IC-engines is that NO_2 is conserved by the freezing of reaction (3) the hot products mix with cooler gases in the combustion chamber. In spark ignition engines the air/fuel charge is premixed and close to stoichiometric. The temperature in the chamber is nearly uniform after the flame has propagated, leading to the NO_2/NO_x ratio being negligibly small <2%. The major part of the combustion occurring in compression ignition engines is mixing controlled. In addition, they operate with an excess of air leading to a wide distribution of cool regions in the chamber. Mixing of hot products with cooler air causes Reaction (3) to quench and NO_2/NO_x levels may reach 10–30%. Nitrous oxide (N_2O) is not formed in significant quantity by combustion of HC in an engine. The main contribution of N_2O emissions from automotive vehicles stem from its production over three-way catalyst during NO_x reduction [12]. However, investigations reveal reaction pathways for the formation of N_2O when NH_3 is in the presence of NO and NO_2 at low temperatures. These reactions are part of the SNCR (selective non-catalytic reduction) mechanism. Under certain conditions, $1000\ K \leqslant T \leqslant 1400\ K$, N_2O levels may be in the vicinity of 30–60 ppm [14].