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# Ignition improvers for aqueous ammonia as marine fuel

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## Abstract

The potential of three molecules  $NH_4NO_2$ ,  $H_2O_2$ , and  $O_3$  to ignite aqueous solutions of ammonia (25% by mass) as fuel, was investigated using chemical kinetic simulations at conditions representative of a two-stroke marine diesel engine. The purpose was to address two of the most prominent issues with making ammonia a practical fuel for marine applications: the difficulty of igniting ammonia, and the safety concerns regarding its volatility and toxicity. The ignition simulations carried out to this end used a two-zone reactor model of the engine, representing the ignition zone into which fuel was injected, and the bulk cylinder gases, respectively. The results suggested that all three ignition improving molecules were able to ignite aqueous ammonia reliably and at high combustion efficiency with acceptable levels of  $NO$ ,  $N_2O$  and  $NH_3$  emissions. Among the three fuel formulations investigated,  $H_2O_2$  in 12% aqueous solution by mass, promised the lowest emissions of  $NO$  and  $N_2O$  in the exhaust gases. This fuel blend added in a mole fraction of 0.15 to 0.85 aqueous ammonia at 25% by mass and promised to be the most practical solution, since it is stable and can be stored safely in a separate tank until injected into the engine.

**Keywords:** Ammonia, Aqueous ammonia, Ignition, Ammonium nitrite, Hydrogen Peroxide, Ozone, Diesel Engine

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## 1. Introduction

The year 2021 was measured to be  $1.11 \pm 0.13$  °C warmer than the pre-industrial baseline (1850-1900) [1]. According to the World Meteorological Organization (WMO), stabilising the global mean temperature to between 1.5 °C and 2 °C within this century will require a strong acceleration of Greenhouse Gas (GHG) reductions before 2030. In 2017 GHG emissions from shipping constituted about 2.97% of total global anthropogenic greenhouse gas emissions [2]. In 2018 the International Maritime Organization (IMO) adopted the 'Initial IMO Strategy on Reduction of GHG Emissions from Ships', agreeing a 50% reduction of the total annual GHG emissions by 2050 with respect to 2008 [3]. In 2023 the IMO is due to revise its Initial Strategy, with proposals being discussed to achieve zero emissions no later than 2050 [4]. Given the typical lifetime of ships being around 25 years, ships ready for zero emissions operation may need to be introduced in the

coming years. Zero-carbon fuels such as ammonia and hydrogen have been high contenders as alternative energy carriers, but concerns regarding the greenhouse gas effect of hydrogen ( $GWP_{100} = 11 \pm 5$  [5]) or the toxicity and difficulty of igniting ammonia are issues yet to be solved. Given the urgent need to deploy zero-carbon fuels in the near future, such fuels should ideally work in existing engine technology, with limited modifications. Among the most prominent challenges for the use of ammonia as fuel for marine diesel engines is its low ignition propensity, which typically results in high unburned ammonia emissions on the order of 2%, and safety concerns regarding the toxicity of anhydrous ammonia. Ammonia fuel is expected to require a high degree of pilot fuel on the order of 5-20% of energy content for large-bore two stroke engines, and possibly up to 40% for medium speed four stroke engines. Such a pilot fuel injection could significantly contribute to the greenhouse gas emissions of ammonia fuelled engines. This work aims to address the ignition difficulties and toxicity of ammonia, by proposing aqueous mixtures of ammonia in combination with ignition improvers that

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do not contain any carbon, as fuel blends to be introduced into existing engine technology. The ability of certain molecules to spontaneously decompose at mild temperatures is used to improve the ignition propensity of diesel fuels. In this case the molecules ammonium nitrite ( $NH_4NO_2$ ), hydrogen peroxide ( $H_2O_2$ ), or ozone ( $O_3$ ) are proposed for initiating the ignition of ammonia in aqueous solution. Anhydrous ammonia requires pressurisation to 0.43 MPa or continuous cooling to 240 K [6], for it to be stored in liquid form. The desire for anhydrous ammonia to dissolve in water makes it dangerous upon inhalation by seafarers or passengers, and suitable safety and personal protection measures will be required in practice. By dissolving ammonia in water (25%  $NH_3$  by mass) aqueous ammonia is formed, which has a boiling point of 311 K at atmospheric pressure, and can thus be bunkered in unpressurised tanks [6]. The addition of water may have advantages, such as decreasing nitrogen oxides ( $NO_x$ ) emissions and potentially increasing cycle efficiency by evaporation [7], provided reliable ignition and combustion can be achieved. The main disadvantages of mixing ammonia with water into aqueous ammonia are that its gravimetric energy density decreases from 18.8 MJ/kg (volumetric  $11341 MJ/m^3$ ) by a factor four to 4.7 MJ/kg (volumetric  $4263 MJ/m^3$ ), and that the difficulty of igniting ammonia is even further compounded by the water, especially if the water needs to be evaporated using heat from the cylinder gases. The energy of aqueous ammonia is between those of lithium-ion batteries of 0.72 MJ/kg (volumetric  $1800 MJ/m^3$ ) [8] and similar to compressed hydrogen at 80 MPa at 120 MJ/kg (volumetric  $5146 MJ/m^3$ ). Aqueous ammonia may thus be suitable on shorter routes and for ships with reduced energy needs, such as those employing wind propulsion to cover part of their energy needs. Şahin et al. (2018) [9] reported the successful combustion of premixed aqueous ammonia with a pilot injection of diesel fuel, though they noted the increase of carbon monoxide ( $CO$ ) and unburned hydrocarbon (UHC) emissions, indicating difficulties with ignition. Pyrc et al. [10] studied the aqueous ammonia with a pilot injection of diesel fuel, reporting longer ignition delays, and deterioration of combustion stability at higher blending fractions, as well as increases in  $CO$  and UHC emissions, but decreased  $NO_x$  emissions. Frost et al. (2021) [11] reported increased ignition delays and  $CO$  emissions with increasing fractions of aqueous ammonia. This work also simulated that aqueous hydrogen peroxide could be used as potential ignition improver for aqueous ammonia and aqueous hydrogen peroxide ( $H_2O_2$ ) suggesting the mixture of 75%  $H_2O$ , 20%  $NH_3$  and 5%  $H_2O_2$  to just about

ignite under the conditions of a small high-speed engine. Independently and earlier, Khalil et al. (2021) [12] reported that the addition of just 2% molar fraction of  $H_2O_2$  decreased the ignition delay of aqueous ammonia by a factor of 30, whilst also resulting in lower nitric oxide ( $NO$ ) emissions. Shafiq et al. (2022)[12] investigated the possibility of reducing ignition delays in a high-speed Homogeneous Charge Compression Ignition (HCCI) engine using hydrogen peroxide ( $H_2O_2$ ). They found that  $H_2O_2$  was very effective in increasing engine load and decreasing  $NO_x$  emissions, when compared with intake air preheating. Singh et al (2022)[13] carried out zero-dimensional chemical kinetic numerical investigations on the ignition delays and laminar flame speeds of ammonia, methane and hydrogen peroxide mixtures. They predicted stark increases in laminar flame speeds and reductions in ignition delays at hydrogen peroxide was added to the mixtures. Further to hydrogen peroxide, ammonium nitrite has been proposed as a carbonless ignition improver for aqueous ammonia and anhydrous ammonia [15, 16], however these two simulation studies employed unusually high cylinder pressures in excess of 25 MPa, which is difficult or currently impossible to achieve without excessive mechanical wear and cylinder scuffing in practice. Using carbonless ignition improvers may be a simple and reliable approach for making aqueous ammonia a safe and practical fuel to be introduced into existing engine technology. This present work aims to address the ignition difficulties and safety of aqueous ammonia by investigating the ability of three potential ignition improvers ammonium nitrite ( $NH_4NO_2$ ), aqueous hydrogen peroxide ( $H_2O_2$ ), and ozone ( $O_3$ ) as additives to ignite aqueous ammonia at temperatures and pressures representative of current marine diesel engine technology. Hydrogen peroxide can be stored and shipped safely as a stable 6.7% mole fraction solution in water (12% m/m), and can be mixed with aqueous ammonia prior to injection. To this end, chemical kinetic simulations were performed at conditions equivalent to an engine operating in service under conventional diesel engine operation on heavy fuel oil (HFO).

## 2. Engine simulation method

The autoignition of aqueous ammonia mixtures with various ignition improvers was simulated using zero-dimensional chemical kinetic reaction models.

### 2.1. Chemical kinetic mechanism

The chemical kinetic mechanism used was that developed by Song et al. (2016) [17]. The mechanism was

extended by the reactions for ammonium nitrite from the mechanism of Izato and Miyaki (2018) [18]. The reaction shown in equation (1) was added to the reaction mechanism.



The gaseous decomposition reaction constant for ammonium nitrite in the engine was assumed to take the form shown in equation 2 below.

$$k = 2.05 \cdot 10^{21} \cdot T^{-2.591} \cdot e^{-\frac{33984 \frac{\text{J}}{\text{kmol}}}{R \cdot T}} \quad (2)$$

The reactions for ozone were added from the ozone sub-mechanism of Halter et al. (2011) [19]. The mechanism of Song et al. (2016) [17] has been validated for pressures of 3-10 MPa and shows reasonable agreement for ammonia combustion at a range of pressures, temperatures and stoichiometries. The autoignition delays of ammonia mixtures with the extended mechanism are shown in Figure 1 against experimental results reported in the literature [20, 21, 22].

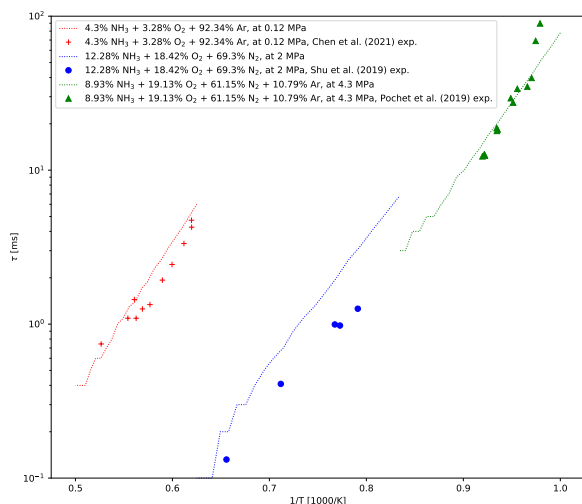


Figure 1: Validation of the chemical kinetic mechanism at various pressures and temperatures.

The simulations show reasonable agreement with the experimental results over a wide range of temperatures (1000-2000 K), and pressures ranging from 0.1-4.3 MPa. The computations were further validated against those of Khalil et al. (2019)[23].

Figure 2 shows that the model used in the current work agrees well with the computations of Khalil et al. (2019)[23].

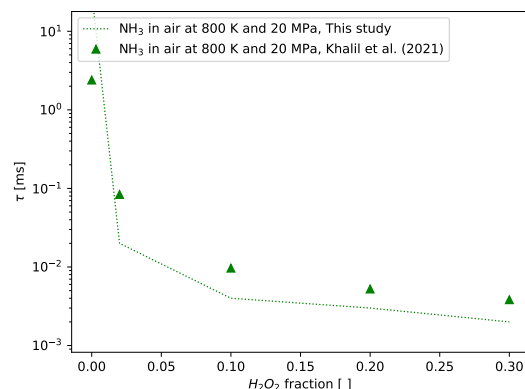


Figure 2: Comparison of the chemical kinetic model with that used by Khalil et al. (2021)[23].

## 2.2. Engine Model

Ignition in the engine was simulated using zero-dimensional chemical kinetic reactor models representing the ignition zone (Zone 1) into which prevapourised fuel was directly injected, and the bulk combustion gases (Zone 2) which were equal in pressure as the ignition zone, but without any mass transfer from the fuel injection taking place into this zone.

The engine simulations were adjusted to match conditions representative of existing engine technology (*MAN B&W 6G50ME – C9.5 – GI* engine) operating in diesel operation on HFO as fuel. These measurements were taken from experimental data recorded on this engine type at sea [24]. The thermodynamic conditions and chemical kinetics were programmed in Python 3.7 [25] using the Cantera software tools [26]. The engine had a 500mm diameter bore, 2.5m stroke, and 2.5m connecting rod length, and operated at a rotational speed of 86 rpm. The scavenging air had a pressure of 0.284 MPa, and a temperature of 413 K, while the fuel was injected at a pressure of 30 MPa and a temperature of 373.15 K. The inlet air consisted of mole fractions of 21 %  $\text{O}_2$  and 79%  $\text{N}_2$ . Fuel injection started at 182° crank angle (2° after piston top-dead-centre), with a constant injection mass flow for a duration of 15° crank angle.

## 3. Ammonium Nitrite

Ammonium nitrite was investigated as ignition improver for aqueous ammonia, engine conditions comparable to those of an existing engine operating in diesel mode on HFO as fuel. The cylinder pressure and

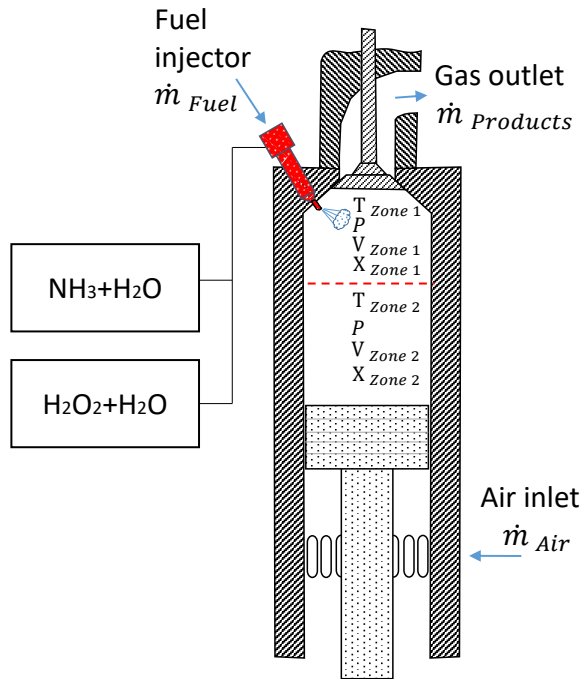


Figure 3: Engine schematic showing the possibility of separately storing aqueous ammonia and aqueous hydrogen peroxide ( $H_2O_2$ ), and mixing them upon injection.

temperature were simulated using the chemical kinetic model for a fuel with molar composition of 25.71%  $NH_3$ , 74%  $H_2O$  and 0.26%  $NH_4NO_2$ , equivalent to every 100<sup>th</sup>  $NH_3$  molecule in the fuel being replaced by  $NH_4NO_2$ .

The cylinder pressure traces shown in Figure 4 allow to compare the original engine operation with that of the simulated cycle operating on aqueous ammonia with ammonium nitrite. The results show that the aqueous ammonia and ammonium nitrite blend ignited under conditions representative of a real engine in terms of pressures and temperatures. A clear difference was visible to the pure aqueous ammonia (without ammonium nitrite,  $NH_4NO_2$ ), which failed to ignite. The calculations also showed that the aqueous ammonia and ammonium nitrite fuel mixture had a visibly longer ignition delay than the engine experiments using HFO as fuel. This is visible in the delay of the peak rate of pressure rise, which occurred around 4° crank angle later for the aqueous ammonia mixture than for the experiments with HFO as fuel.

Figure 5 shows that the cylinder temperature initially dropped in the ignition zone upon fuel injection. This

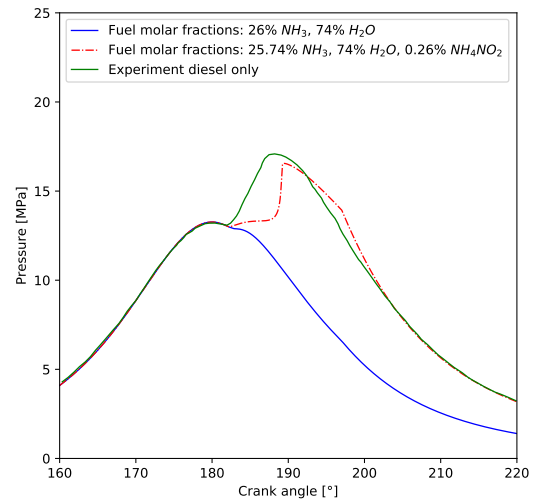


Figure 4: Cylinder pressure for aqueous ammonia and aqueous ammonia with  $NH_4NO_2$  as ignition improver, compared with a conventional experimentally measured pressure trace on heavy fuel oil.

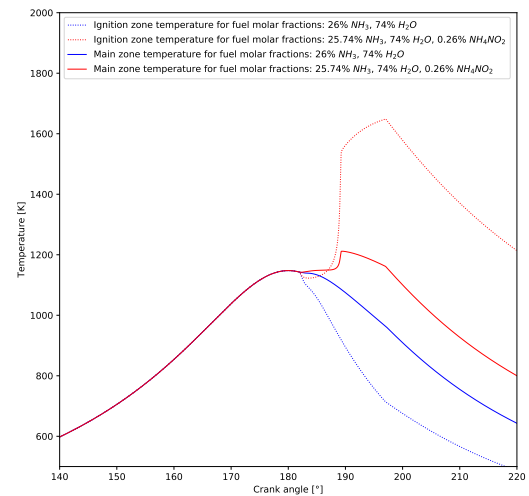


Figure 5: Variation of reaction temperatures in ignition zone (Zone 1) and the zone of the bulk cylinder gases (Zone 2) for aqueous ammonia with  $NH_4NO_2$  as ignition improver.

was the case for both aqueous ammonia and aqueous ammonia with  $NH_4NO_2$ . In the case of pure aqueous ammonia the temperature kept dropping steeply until fuel injection was completed, after which it dropped at a lower rate, due to the continuing expansion of the gases. The water present in the aqueous ammonia obviously

compounded the problem of cooling the ignition zone with water, making ignition even more difficult than for anhydrous ammonia [15]. In the case of aqueous ammonia with  $NH_4NO_2$ , the temperature within the ignition Zone 1 dropped initially, but then increased once ignition began. The heat release and expansion of gases in Zone 1 also resulted in an increase of the temperature of the bulk gases in Zone 2, by compression and by heat transfer. Figure 6 shows the simulated traces of mole fractions of chemical species relevant to the ignition of aqueous ammonia.

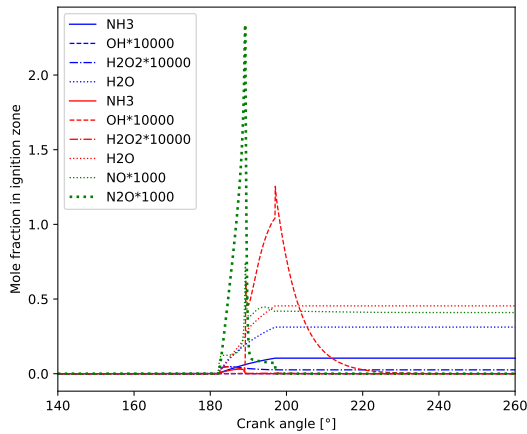


Figure 6: Mole fraction of chemical species for aqueous ammonia and aqueous ammonia with  $NH_4NO_2$  as ignition improver.

The results show that for pure aqueous ammonia as fuel, ammonia accumulated in the ignition zone without being consumed. Aqueous ammonia with ammonium nitrite on the contrary, was almost entirely consumed, indicating a high efficiency of combustion. Figure 6 shows that the moment of high pressure increase is marked by the formation of hydroxyl ( $OH$ ) radicals, which later decomposed again. Prior to the formation of  $OH$  radicals,  $N_2O$  was formed, which later almost entirely decomposed, leaving only a mole fraction of 84.6 ppb  $N_2O$  at  $260^\circ$  crank angle. The fraction of  $NO$  in the exhaust gases was 4.1 ppm for aqueous ammonia ignited with  $NH_4NO_2$ . This was the highest fraction of  $NO$  for any of the three ignition improvers used in this study. Although  $NH_4NO_2$  added nitrogen atoms to the ignition zone, most of the additional  $NO$  formed was likely to be the result of thermal  $NO$  formation due to the higher combustion temperatures of almost 1700 K.

#### 4. Hydrogen peroxide in aqueous solution

The ignition of aqueous solution of ammonia 25% (m/m) mixed with a 12% (m/m) aqueous solution of hydrogen peroxide was investigated under typical marine diesel engine operating conditions. The mole fraction of the fuel mixture consisted of 0.85 aqueous ammonia and 0.15 aqueous hydrogen peroxide, yielding a final fuel composition of molar fractions 22.1%  $NH_3$ , 1.0%  $H_2O_2$ , and 76.9%  $H_2O$ .

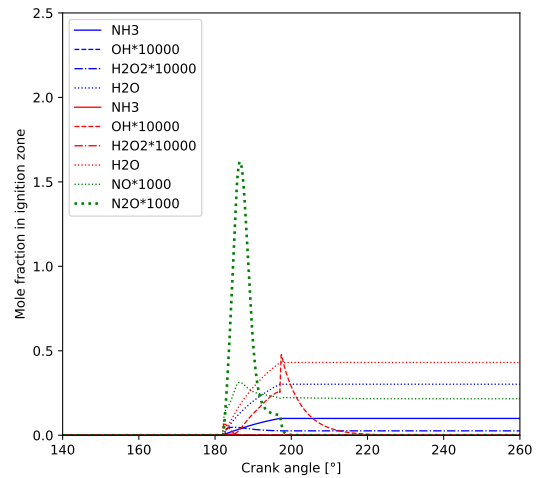


Figure 7: Cylinder pressure for aqueous ammonia and aqueous ammonia with  $H_2O_2$  as ignition improver, compared with a conventional experimentally measured pressure trace on heavy fuel oil.

Figure 7 shows that the mixture of aqueous ammonia and aqueous hydrogen peroxide were simulated to ignite with a short ignition delay. The fast reactions provided a cylinder pressure trace similar to the measured pressure trace of the diesel engine operating on HFO. Figure 8 shows that the temperature at which ignition took place was around 1130 K.

The short ignition delay of this fuel meant that the temperature started rising rapidly in Zone 1 following the start of fuel injection. The temperature was simulated to rise to almost 1600 K for the reacting gases in Zone 1, and for the bulk cylinder gases in Zone 2 to around 1250 K. For pure aqueous ammonia, the chemical kinetic calculations predicted that aqueous ammonia would not ignite. In Zone 1 fuel injection merely resulted in cooling the ignition zone mixture, which dropped further but at a lower rate after the end of fuel injection, due to the expansion of the cylinder. The short ignition delay of aqueous ammonia with aqueous hydrogen peroxide on the contrary, suggested that this fuel

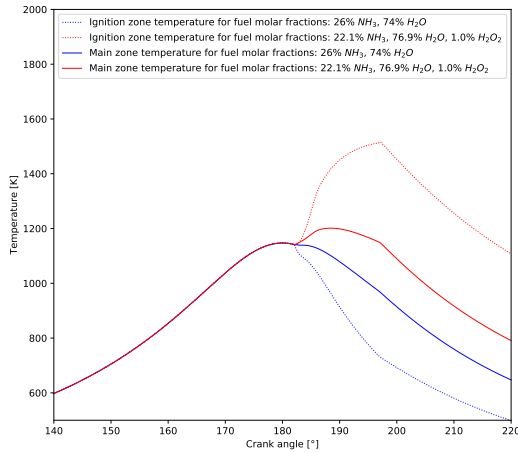


Figure 8: Variation of reaction temperatures in ignition zone (Zone 1) and the zone of the bulk cylinder gases (Zone 2) for aqueous ammonia with  $H_2O_2$  as ignition improver.

mixture may be adequate for achieving reliable ignition at conditions of 13 MPa and 1130 K, which were the conditions simulated close to piston top-dead-centre.

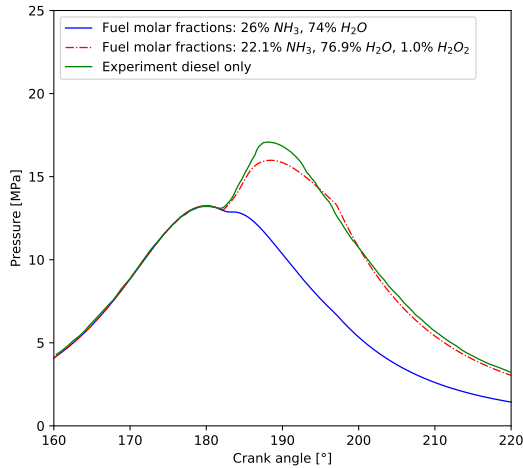


Figure 9: Mole fraction of chemical species for aqueous ammonia and aqueous ammonia with  $H_2O_2$  as ignition improver.

Figure 9 shows the molar fractions of various chemical species in Zone 1 during the ignition process. From the moment of injection of the fuel the species  $NH_3$ ,  $H_2O_2$ ,  $N_2O$  and  $NO$  appeared in Zone 1. A progressive increase in  $OH$  radicals followed, which peaked markedly just after fuel injection ceased. The com-

bustion process was essentially complete around  $220^\circ$  crank angle, and at  $260^\circ$  crank angle a mole fraction of only  $3.9 \cdot 10^{-14}$  of  $NH_3$  remain in the gases, indicating a high degree of conversion of the fuel.

#### 4.1. Ignition delay map for mixtures of aqueous ammonia with aqueous hydrogen peroxide

An insight into the ignition delays of aqueous ammonia with aqueous hydrogen peroxide was obtained over a range of fuel compositions and temperatures to develop an ignition delay map. The ignition delays of this fuel blend were calculated for other molar fractions than the 0.85 aqueous ammonia 25% (m/m) and 0.15 aqueous hydrogen peroxide 12% (m/m) used in the engine simulations of section 4, and for temperatures ranging from 900 K to 1300 K. The ignition delays were calculated assuming a constant pressure ignition and combustion process at 12.5 MPa.

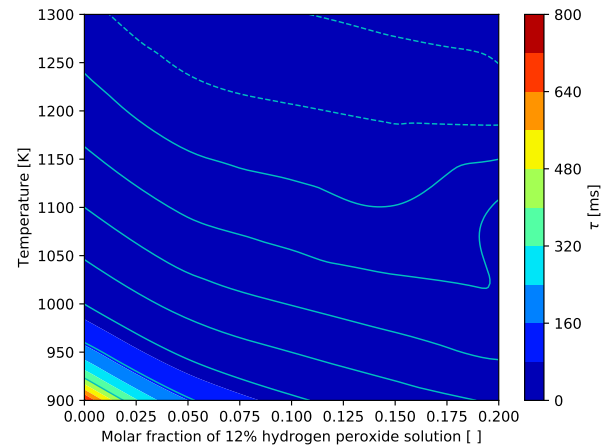


Figure 10: Ignition delay  $\tau$  [ms] for aqueous ammonia mixtures with 12% m/m aqueous  $H_2O_2$  solution.

Figure 10 shows that the longest ignition delays were observed at low temperatures, for pure aqueous ammonia with no hydrogen peroxide added. For higher temperatures, the ignition delays became lower for all mixtures. For mole fractions having at least 0.10 aqueous hydrogen peroxide 12% (m/m), the ignition delay was reduced to below 80 ms at all temperatures down to 900 K. Since ammonia is a nitrogen-containing fuel, the formation of nitric oxides and nitrous oxides is a concern for marine diesel engines using this fuel. The formation of these two chemical species was thus mapped over the same conditions as used in Figure 10.

Figure 11 shows the mole fraction of  $NO$  in the products gases. The mole fraction of  $NO$  increased for higher ignition temperatures, and decreased for higher

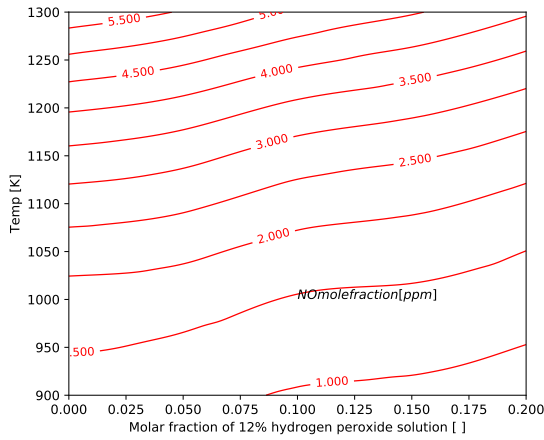


Figure 11:  $NO$  mole fraction [ppm] for aqueous ammonia mixtures with 12% m/m aqueous hydrogen peroxide solution.

fractions of  $H_2O_2$  present in the fuel. The increase in  $NO$  formation at higher temperatures could be explained by thermal  $NO$  formation. The decrease of  $NO$  with higher fractions of  $H_2O_2$  may be due to the addition of further water to the fuel mixture. This finding is reassuring in that it suggests that the addition of aqueous  $H_2O_2$  would not result in increasing  $NO$  emissions.

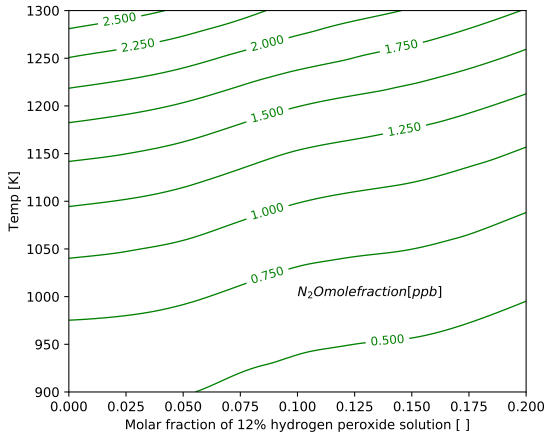


Figure 12:  $N_2O$  mole fraction [ppb] for aqueous ammonia mixtures with 12% m/m aqueous hydrogen peroxide solution.

Nitrous oxide ( $N_2O$ ) is a potent greenhouse gas with a 100-year Global Warming Potential of  $GWP_{100} = 273$  [27]. Avoiding its formation in the exhaust gases of marine diesel engines using ammonia as fuel is thus of particular interest, in order to keep the greenhouse gas

emissions from use of this fuel low. Figure 11 shows the mole fraction of  $N_2O$  in the exhaust gases over the same conditions as used in Figure 10. The results showed that the lowest mole fraction of  $N_2O$  was formed at the lowest temperatures and with higher fractions of  $H_2O_2$  as ignition improver. Using a mole fraction of 0.06 aqueous hydrogen peroxide solution (12% m/m) allowed to produce less than 1 ppb of  $N_2O$  in the product gases. Determining the exact values of  $N_2O$  emissions from this fuel mixture will require experimental measurements and validations, but the present computations should provide a reasonable indication of the trends that may be expected.

## 5. Ozone as potential ignition improver

The addition of ozone ( $O_3$ ) as ignition improver at a mole fraction of 0.26%  $O_3$  in aqueous ammonia of 25.74%  $NH_3$  and 74%  $H_2O$  was investigated for the same engine operating conditions as ammonium nitrite and hydrogen peroxide.

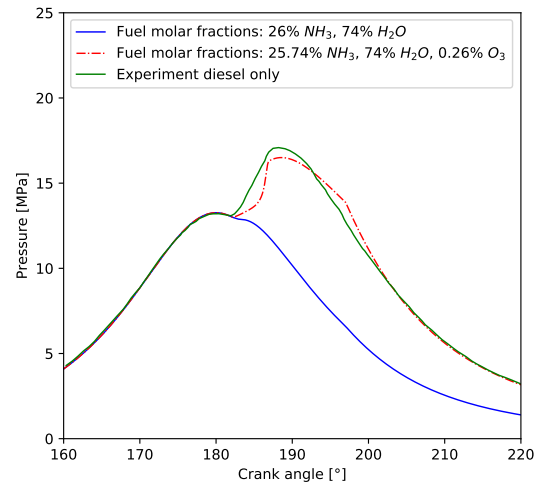


Figure 13: Cylinder pressure for aqueous ammonia and aqueous ammonia with  $O_3$  as ignition improver, compared with a conventional experimentally measured pressure trace on heavy fuel oil.

Figure 13 shows that the addition of  $O_3$  achieved ignition of aqueous ammonia with a reasonably short ignition delay, resulting in a pressure trace that was reasonably similar to the measurements of the engine operating on HFO. The ignition delay was visibly shorter than for the simulations employing  $NH_4NO_2$  as ignition improver at the same mole fraction. This suggested that at



the same mole fraction,  $O_3$  is more effective as ignition improver than  $NH_4NO_2$ .

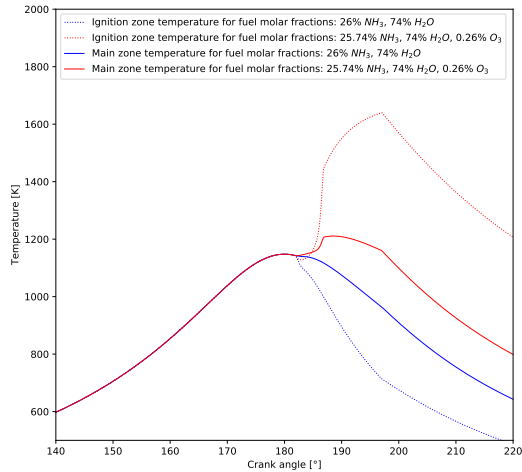


Figure 14: Variation of reaction temperatures in ignition zone (Zone 1) and the zone of the bulk cylinder gases (Zone 2) for aqueous ammonia with  $O_3$  as ignition improver.

Figure 14 shows the temperature for in the ignition zone (Zone 1) and the bulk cylinder gases (Zone 2). The traces show that the temperature in the ignition zone dipped slightly before recovering and increasing steeply during ignition for aqueous ammonia with  $O_3$  as ignition improver. The temperatures in Zone 1 reached temperatures above 1600 K before fuel injection stopped.

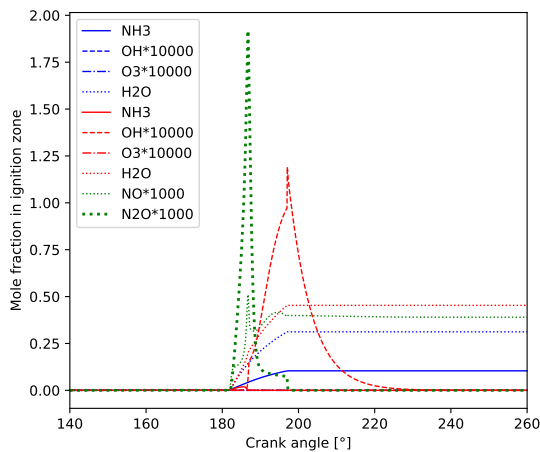


Figure 15: Mole fraction of chemical species for aqueous ammonia and aqueous ammonia with  $O_3$  as ignition improver.

Figure 15 shows the mole fraction of chemical species during the ignition and combustion sequence for aqueous ammonia with  $O_3$  as ignition improver. The results show that the formation of nitrous oxide and nitric oxide were almost as strong as for  $NH_4NO_2$  as ignition improver, and that their peak mole fractions were followed by a peak in  $OH$  radicals around the time when fuel injection finished. As for the previous two ignition improvers, combustion of  $NH_3$  was completed to a high degree when the ignition improver was used, whereas during operation on pure aqueous ammonia without ignition improver almost all of the injected  $NH_3$  remained unburned in Zone 1.

## 6. Direct comparison of ignition improvers

In order to provide a direct comparison of the effectiveness of the three ignition improving molecules on shortening the ignition delay of the fuels in air, simulations were conducted in a constant pressure reactor changing only the ignition improving molecule in the reactants.

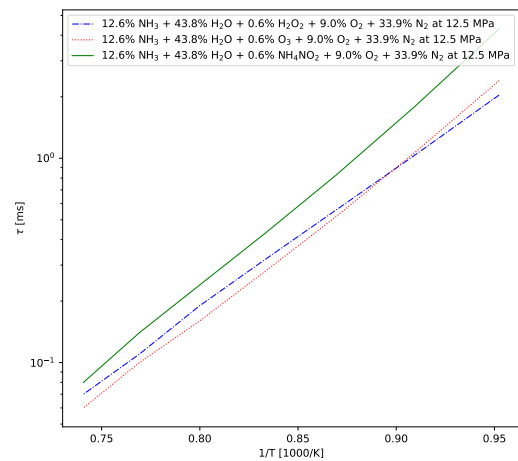


Figure 16: Direct comparison of ignition improvers at constant pressure (12.5 MPa) conditions and varying temperatures.

The results in Figure 16 show that at ignition temperatures below 1100 K,  $H_2O_2$  was the most effective ignition improver, followed by  $O_3$  and  $NH_4NO_2$ . At temperatures above 1100 K,  $O_3$  was observed to be the most effective ignition improver.

## 7. Summary and Conclusions

This work aimed to address two salient issues with making ammonia a practical fuel for marine applications: First the difficulty to ignite ammonia, and second the high safety risks related to the toxicity of ammonia. These two issues were addressed by investigating the ability of three potential ignition improvers. The ignition improvers were applied to aqueous ammonia rather than to anhydrous ammonia in order to increase safety of the fuel and reduce its volatility and desire to dissolve in water. The three ignition improvers consisted of ammonium nitrite ( $NH_4NO_2$ ), aqueous hydrogen peroxide ( $H_2O_2$ ) in the form of a safe and stable 1% mole fraction solution in water (12% m/m), and ozone ( $O_3$ ). The ignition was simulated using thermodynamic and chemical kinetic calculations at temperatures and pressures representative of existing marine diesel engine technology. The simulation results suggested that all three ignition improving molecules were successful in igniting aqueous ammonia under typical conditions of a marine diesel engine, with the temperature around piston top-dead-centre at 1130 K and pressure around 13 MPa. Small differences distinguished the three ignition improvers in terms of their combustion characteristics:  $NH_4NO_2$  produced slightly higher NO in the exhaust gases than  $O_3$ , whereas  $O_3$  produced slightly higher  $N_2O$  emissions than  $NH_4NO_2$ . A structured overview of the  $NO$ ,  $N_2O$ , and  $NH_3$  emissions for the three potential ignition improvers is provided in Table 1.

Table 1. Mole fractions of various species present in the exhaust gas of the engine when using the three ignition improvers.

		Ignition improver		
		$NH_4NO_2$	$H_2O_2$	$O_3$
Mole fraction in exhaust	$NO$	4.1 ppm	2.1 ppm	3.9 ppm
	$N_2O$	84.6 ppb	0.2 ppb	86.2 ppb
	$NH_3$	$2.1 \cdot 10^{-14}$	$3.9 \cdot 10^{-14}$	$2.1 \cdot 10^{-14}$

Using  $H_2O_2$  as 12% (m/m) aqueous solution as ignition improver resulted in the lowest  $N_2O$  and  $NO$  emissions amongst the three ignition improvers. This may partly be owed to the additional water added along with the  $H_2O_2$ , which acted as an inert substance lowering the peak combustion temperatures.  $H_2O_2$  in aqueous solution also had a slightly higher emission of  $NH_3$  in the exhaust gases, indicating a lower combustion efficiency, but since the  $NH_3$  emissions were very low for all three ignition improvers, and  $NH_3$  emissions are generally less problematic than  $N_2O$  emissions, this may be an issue that could be acceptable. In addition

to the gas-phase combustion characteristics investigated in this work,  $H_2O_2$  also appears to be the most practical solution among the three ignition improvers investigated, since  $H_2O_2$  is available as a 12% (m/m) stable aqueous solution that can be carried safely on a ship alongside aqueous ammonia, as long as these are kept in two separate tanks. The idealised chemical kinetic simulations reported herein are a necessary initial step in guiding real engine experiments. The results provide a promising indication of the potential of these ignition improvers to make ammonia a viable fuel for existing engine technology. Practical engine tests will still be necessary to physically verify and measure the ability of these ignition improvers to provide reliable ignition at marine diesel engine conditions.

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