# Plasma reforming of ammonia for improved combustion performance

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**Abstract:** Ammonia is a promising fuel for future energy applications. However, its use in combustion engines is limited by poor burning properties. This study experimentally explores the kinetics of nanosecond repetitively pulsed plasma reforming of ammonia for  $H_2$  generation in a novel well-stirred reactor with a double dielectric barrier discharge under a range of applied voltages, pulse repetition frequencies, flow residence times, and operation duty cycles. Results indicate up to 3.5%  $H_2$  yield using approximately 200 W plasma power.

Keywords: Ammonia, plasma reforming, nanosecond repetitively pulsed discharge.

# 1. Introduction

The 2021 IPCC report asserted that drastic reduction in CO<sub>2</sub> emissions by 2030 is imperative for remaining below the Paris Climate Accords target of keeping warming to below 1.5°C [1]. This will require a large scale move to renewable energy at an accelerated pace, adapting existing power and transportation infrastructure and employing modular power production. Hydrogen production from renewable energy is currently being implemented as a method of excess energy storage [2]. However, hydrogen is difficult and expensive to store for long periods, as well as to ship and carry on board as a fuel. Ammonia is a cheap and effective hydrogen carrier with higher volumetric energy density than liquified H<sub>2</sub> at moderate storage conditions. As a comparison, ammonia storage costs are 26 to 30 times cheaper than hydrogen [2]. Synthesis of ammonia from green hydrogen is already replacing fossilfuel based hydrogen sources [3], and less energy intensive ammonia synthesis techniques to replace the Haber-Bosch process is an active area of research [4]-[7]. Because of the widespread use of ammonia in agriculture and in the chemical industry, well-established storage, delivery, and handling methods already exist. The produced ammonia can be transported and then converted back to hydrogen, or directly used as a fuel for various applications, including energy generation and in transportation applications, using fuel cells or combustion engines.

For combustion applications, pure ammonia has poor qualities when compared to hydrocarbons. Ammonia combustion generates high NO<sub>x</sub> emissions, and is incompatible with existing engines due to low flame speed (~7 cm/s) and resistance to ignition. To use ammonia as a combustion fuel would then require one of two approaches: re-design engines to mitigate the deficiencies of ammonia [8]–[10], or alter the fuel properties to improve performance without significantly changing engine design. The latter approach would allow ammonia to be used in current infrastructure, as well as require only minimal changes to future engine designs, reducing the cost of a transition to the zero-carbon fuel. In our current studies, plasma-reforming to modify the ammonia fuel stream composition and yield hydrogen and/or a mixture of hydrogen and other plasma-produced species is explored, both numerically and experimentally.

In Faingold and Lefkowitz [11], a stoichiometric mixture of  $NH_3$  and  $O_2$ , with 75% He dilution, was simulated in a 0-D intermediate-temperature (initial temperature of 1500

K – above the autoignition temperature of ammonia) plasma, using an in-house modelling tool. For this purpose, a kinetic model was assembled, and low energy discharges with  $5 \times 10^{-5}$  J cm<sup>-3</sup> energy deposition per pulse and 180 Td reduced electric field (representing a large-volume DBD) at pulse repetition frequencies (PRFs) of up to 1 MHz were deposited. It was found that up to 90% reduction in the ignition delay time was possible as compared to an equal energy deposition of thermal energy. In addition, it was found that the initial temperature needed for autoignition (assuming 10 ms maximum ignition delay time) could be reduced to 300 K even for the low energy discharges, provided PRFs of 1 MHz. Generation of radical species in the plasma, particularly atomic H and atomic O from electron collision dissociation reactions, greatly enhanced the rates of the pre-ignition induction chemistry, allowing for auto-ignition with relatively little energy channelled into increasing the translational temperature of the heavy species.

Following this work, Faingold et al. [12] extended the numerical model to include N<sub>2</sub>. This study implemented a low-temperature plasma (initial temperature of 300 K) as a reforming mechanism, and explored its impact an autoignition in a simulated 50 bar, 1000 K environment. Pulsed plasma with  $5 \times 10^{-4}$  J cm<sup>-3</sup> energy per pulse applied at 200 kHz PRF was found to reform enough of the mixture (stoichiometric NH<sub>3</sub>/air) in 5 ms to reduce the ignition delay time by a factor of 50. Interestingly, the final NO concentration after ignition was reduced by a factor of 25. These improvements are mainly attributable to the presence of  $H_2$  in the reformate stream, with a secondary benefit from NH<sub>2</sub> radical. An increase the path flux through  $NO + HO_2 \rightarrow NO_2 + OH$  was found to majorly increase the OH concentration, contributing to faster NH<sub>3</sub> consumption. In addition, increased presence of NH<sub>2</sub> helped to reduce the NO concentration via NO + NH<sub>2</sub>  $\rightarrow$  NNH + OH and NO +  $NH_2 \rightarrow N_2 + H_2O.$ 

At the time of its publication, the numerical works by Faingold et al. [11], [12] could not be validated due to a lack of experimental data in the literature. While recent works by Bang et al. [13] and Zhong et al. [14] have since emerged, which include experimental measurements of ammonia oxidation, the present study aims to create a wide-ranging dataset to fully validate the above-discussed models for conditions specific to plasma-reforming. In addition, experimental proof of the yields and efficiencies possible using plasma reforming of pure ammonia and ammonia/air mixtures can support continued exploration of this concept as a practical alternative to other reforming methods, namely thermal or catalytic reforming.

## 2. Experimental Methods

A well-stirred reactor using a double dielectric barrier discharge (DBD) configuration to create a uniform discharge was constructed for the purposes of this study. A schematic of the experimental apparatus is presented in Figure 1, with an image of the reactor in operation. The reactor is constructed of a fused-silica bulb with outer diameter of 4 cm and length of 4 cm, with the high-voltage mesh electrode outside of the reactor wall. The inner electrode is a stainless steel rod contained inside an alumina dielectric sheath. The inlet streams are arranged to create an environment with fast mixing of the reactants with the gases already present in the reactor. The plasma is generated using a nanosecond-pulsed high-frequency power supplies, enabling a range of high voltage (1-20 kV) and/or high-frequency (1 - 200 kHz) discharges to explore, with pulse width of 5-6 ns FWHM. The reactor pressure was maintained at 85 Torr, and residence time and duty cycle are varied. At present, only GC-TCD measurements of H<sub>2</sub> yield are available. Measurements of temperature via optical emission spectroscopy (OES) of the N2 2nd-positive system are underway, as well as direct ICCD imaging to confirm plasma uniformity. An example OES spectrum for conditions of 10 kV peak voltage, 10 kHz PRF plasma is presented in Figure 2, along with a long-duration image of the plasma at the same conditions.



Fig. 1. Schematic of the well-stirred plasma reactor experimental setup.



Fig. 2. Plasma uniformity for a plasma pulse frequency of 10 kHz and 10 kV, at 77 Torr (inset), and measured spectra by OES of N<sub>2</sub>(C-B) transition (black line) and fitted data (blue line) corresponding to the same plasma

conditions. The measured rotational temperature for these conditions was 319 K.

# 3. Results

Reforming of pure ammonia is explored for conditions of peak voltage from 12 - 20 kV, and PRFs from 1 - 50kHz. These conditions were selected to provide a relatively uniform plasma discharge with continuous plasma deposition, which limited the maximum PRF for a given peak voltage. The percent of H<sub>2</sub> present in the reformate gas as a function of PRF for three voltage values is presented in Figure 3. Residence time in the stirred reactor is 40 ms. An approximately linear relationship between PRF and H<sub>2</sub> yield is found for each peak applied voltage, indicating that, at these conditions, no pulse-to-pulse coupling effects are present. Maximum H<sub>2</sub> yield for these conditions is approximately 2.5% (for the 15 kV case at 40 kHz PRF), which is far in excess of the 8000 ppm which previous modelling [12] indicated is enough conversion to reduce ignition delay time by two orders of magnitude at realistic IC engine conditions. This amount of reforming is achieved using approximately 200 W of power deposition. Accurate energy measurements are presently underway. There is a clear trend of increasing H<sub>2</sub> yield with increasing applied voltage, however, this does not significantly increase the maximum H<sub>2</sub> yield as higher voltages are accompanied by lesser maximum PRF to maintain a uniform discharge.



Fig. 3. Percentage of  $H_2$  in the reformed gas as a function of PRF for three peak voltage conditions. Reactor conditions: pure NH<sub>3</sub>, P = 85 Torr, T<sub>i</sub> = 290 K,  $\tau_{res}$  = 40

To explore the effect of residence time, the plasma condition was set to a moderate condition of 15 kV peak voltage and 20 kHz PRF. The residence time was varied from 40 - 80 ms. Results are presented in Figure 4. Over a factor of two increase in the residence time, the H<sub>2</sub> yield more than tripled. While this may indicate some synergistic effect of the plasma with a long residence time in the reactor, further experiments as well as model comparisons are needed to confirm this trend. In a study by Lhuillier et al. [15] in a spark ignition engine, it was found that 5% NH<sub>3</sub> conversion to H<sub>2</sub> was enough to ensure stable operation

over a range of equivalence ratios. Thus, even in the nonoptimized reactor presented herein, the amount of conversion required to run an IC engine is approached.



Fig. 4. Percentage of  $H_2$  in the reformed gas as a function of residence time. Reactor conditions: pure NH<sub>3</sub>, P = 85 Torr, T<sub>i</sub> = 290 K, V<sub>peak</sub> = 15 kV, PRF = 20 kHz.

To assess the possibility of higher voltage and frequency combinations without generating plasma instabilities, a duty-cycle energy deposition approach was explored. The results are presented in Figure 5, all using 15 kV peak voltage. Four 50 kHz PRF conditions were selected, one with 10 pulses applied and then 15 pulses skipped, one with 20 pulses applied and then 30 pulses skipped, one with 5 pulses applied and 20 pulses skipped, and one with 10 pulses applied and 40 pulses skipped. The first two cases both averaged to 20,000 pulses per second (20 kHz). As such, they can be compared to the 20 kHz continuouslypulsed case. While the 20 on, 30 off duty cycle resulted in slightly less yield than continuous pulsing, the 10 on, 15 off duty cycle more than tripled the H<sub>2</sub> yield. This points to a non-linear optimization in the reactor operation. As our pulsed-discharge device can be operated up to 200 kHz in duty-cycle mode, further exploration is warranted. A similar trend was not observed for 10,000 pulse/second operation.





#### 4. Conclusions

This study explored  $H_2$  yields in a newly constructed double-DBD well-stirred plasma reactor. Initial results indicate that peak voltage operation up to 20 kV can increase  $H_2$  yield as compared to lower voltage operation (12 or 15 kV). In addition, for a fixed peak voltage, PRF was found to linearly increase the  $H_2$  yield up to 50 kHz. Increasing residence times (from 40 up to 80 ms) and duty cycle operation (allowing higher peak voltage/PRF combinations) found non-linear improvement in the  $H_2$ yield, indicating the possibility of synergistic pulse-topulse coupling behaviour in the reactor.

These results provide the first parametric exploration of nanosecond repetitively pulsed DBD reforming of ammonia. Further work to specify the reactor temperature, confirm the uniformity of the plasma, and accurately measure energy deposition are underway. Future plans include expanded species measurements, as well as a broader parametric range including pressure and initial temperature in the reactor. Model comparisons will assess the present ability to predict reactor performance.

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