2021-2022 Grand Challenge Award Final Report

Awardee: **Laxminarayan L. Raja, Professor**
Aerospace Engineering & Engineering Mechanics

Research Award Title: **Modeling of Cold Plasma Discharge for the Activation of Ammonia as a Carbon-free Liquid Fuel**

Research Summary

Ammonia is a special chemical that finds a wide range of applications ranging from fertilizer production to use as nitrogen source in specialty manufacturing industry, e.g. in the semiconductor industry. A number of new applications have been proposed, for example ammonia as a carbon-free liquid fuel, albeit with low calorific value and poor burning characteristics compared to traditional hydrocarbon fuels.

Cold (low-temperature) plasmas can be used both for the production of ammonia from constituent gases (global reaction: $N_2 + 3H_2 \rightarrow 2NH_3$), or in the decomposition of ammonia into its constituents (global reaction: $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2$) where desired. The latter decomposition process can be thought of as a preliminary step (i.e. "fuel preparation" step) to activate the ammonia prior to its combustion with air for example, thereby improving its combustion characteristics, i.e. its flame speed. In order for a cold plasma to be effective as an ammonia fuel preparation step, it must be highly energy efficient in the production of radicals such as N, H and intermediates such as N_xH_y.

In this work we develop a high-fidelity simulation of a cold-plasma based ammonia decomposition process for ammonia activation in combustion. Microwave generated cold plasmas are typically the most energy efficient sources for decomposing high pressure molecular gases. Here, the microwave excitation can be used to efficiently generate a low electron temperature plasma that acts preferentially to decompose molecular bonds; rather than ionizing the gas. For the ammonia fuel activation application, a remote microwave source fed by a waveguide that wraps around dielectric tube that carries the ammonia gas is proposed. Figure 1 represents a schematic of the device along with the 3D computational mesh used for the simulations performed in our study. Dimension of the device are indicated in Figure 1.

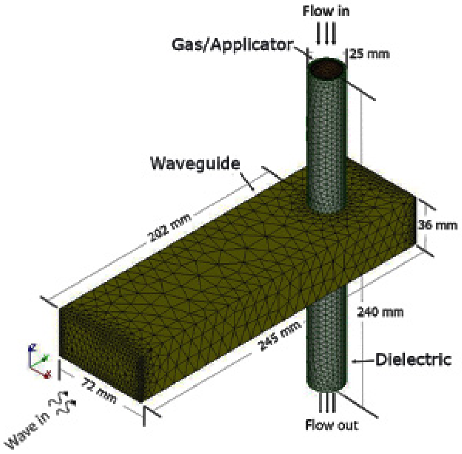

Figure 1: 3-D schematic and computational mesh of apparatus

The computational model represents governing equations of a non-equilibrium cold plasma that include species continuity equations for all relevant chemical species (neutral and charged) in the plasma with a quasi-neutral constraint for the electrons, the electron temperature, the Navier-Stokes equation for the flow, and Maxwell's equation for the microwave field in the waveguide and in the gas tube.

A comprehensive plasma chemical reaction mechanism was developed, based on input from the literature. The mechanism consists of 23 species and 151 reactions; the species represented being e, $NH_3, NH_3^+, NH_4^+, NH_2, NH_2^+, NH_2^-, NH, NH^+, N, N^+, N_2, N_2^+, H, H^+, H^-$, $H_2, H_2^+, H_3^+, N_2H_2, N_2H_3, N_2H_4$ and $NH_3(v)$.

Baseline simulations were performed for a reference condition of 520 Pa (~3.9 Torr) and a mixture of NH_3 (0.25 mole fraction) and N_2 (0.75 mole fraction) that enters the tube with a mass flow rate of $8.95 \times 10^{-}5\frac{kg}{s}$ (corresponding to 3.9 slm of N_2 and 1.3 slm of NH_3). Note the nitrogen gas is used as a diluent to stabilize the computational simulations, used as a preliminary reference condition to stabilize the simulations. Power introduced by the EM wave is set at 2.8 kW. Also, gas temperature at the inflow is set at 300 K. A TE_{10} polarized microwave enters the waveguide with a frequency of 2.45 GHz. Finally, initial species densities for NH_3 and N_2 were calculated following the ideal gas law with the temperature and pressure stated above, while the seed concentrations for all other species (including electrons) was set at $10^9 m^{-3}$.

Figure 2 shows microwave propagation within the gas flow tube, indicated by the wave E-field, the absorbed microwave power into the plasma, the resulting the electron temperature, and the gas temperature resulting from the electron-to-gas collisional energy loss. For easy visualization, slices normal to the X and Y cut planes in the gas tube are shown. Note that the flow is from top to bottom in the figure. The wave E-field indicated a prominent surface wave propagation mode that starts at the location of the intersection of the waveguide with the tube and propagating in both upstream and downstream directions. The electron temperature reaches a peak of about 4 eV with net gas heating resulting in peak temperature of about 880 K.

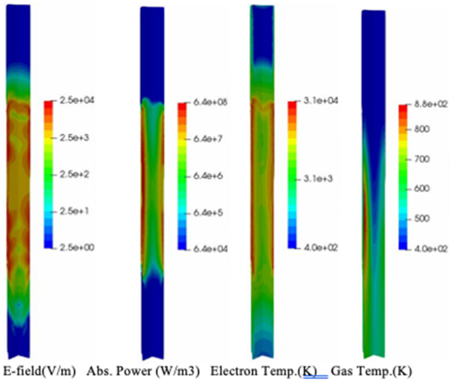

Figure 2: Wave field, wave absorbed power, electron and gas temperature profiles in the gas tube.

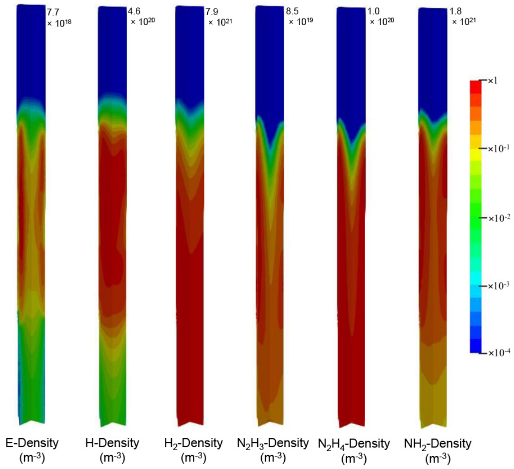

Figure 3: Dominant plasma and radical species in the gas.

Figure 3 shows the results obtained for the electron density and important radical species densities in the microwave generated plasma. All of the plasma activity is limited to the location where the waveguide intersects the gas tube where wave power is deposited into the gas. Peak electron density approaching $10^{19} m^{-3}$ is seen in an annular region adjacent to the gas tube wall. The radial density profile exhibits a hollow core owing to wave shielding by the rather density plasma and the axial gas transport down the tube.

Important radical species produced by the plasma include H, NH_2, N_2H_3, and N_2H_4. In addition, stable decomposition product of H_2 is also seen in the tube. The nitrogen is largely tied up in the radical species rather than as the stable dimer N_2. The peak H radical density is about $4.2 \times 10^{20} m^{-3}$ and is relatively confined to the plasma wave heating zone. As this radical is carried downstream it rapidly recombines to form H_2 which exits the tube. Of the remaining dominant N_xH_y radicals NH_2 is the most dominant with a peak density of about $10^{21} m^{-3}$. Most importantly, the radicals and as well as the stable product H_2 are transported efficiently out the tube where they can be used to influence subsequent gas processes, e.g. the enhancement of ammonia combustion.

Outcomes and benefits

The release time afforded by the Moncrief Grand Challenge grant allowed the PI to mentor graduate students in the development and conduct of this research. In particular, two graduate students were mentored, one on the development of the ammonia plasma chemistry and the other on the development of the plasma discharge model. Activities in this project are synergistic with an ongoing activity on a PSAAP3 project at the Oden Institute, where high-fidelity models for a glow discharge plasma and an inductive torch plasma are being pursued.

Publications

- J.P. Barberena and L.L. Raja, “3D modeling study of remote microwave NH3/N2 plasma for wafer native oxide cleaning process,” journal article in preparation.

Presentations made

- J. P. Barberena and L. L. Raja, “A 3D model of a remote microwave NH3/N2 plasma,” presented at the Gaseous Electronics Conference, Sendai, Japan, Nov. 2022 (virtual).
- J.P. Barberena, N. Murugesan, and L.L. Raja, “Remote plasma generation of radicals for multistream chemical kinetics studies, paper presentation at AIAA SciTech 2022 (virtual).