Evaluating Nitrogen Solubility in Nitrous Oxide and its Potential Effects on Combustion

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This paper describes combustion experiments performed with nitrogen-nitrous oxide mixtures and the potential effects that mixing nitrogen in nitrous oxide may have on bipropellant combustion. The goal is to determine whether pressurizing a nitrous oxide tank with nitrogen will cause sub-optimal combustion to occur during flight. First, the rate at which nitrogen mixes with nitrous oxide at varying pressures and temperatures is evaluated. Next, the combustion instabilities caused by inert gases in the combustion chamber are discussed. Finally, the effects of multiple molar ratios of nitrogen dissolved in nitrous oxide on nitrous oxide decomposition are analyzed, as well as the effects of the combination of nitrogen and hydrocarbons on the decomposition of nitrous oxide. The conclusion on whether it is advisable to pressurize a nitrous oxide system with nitrogen is highly dependent on the factors discussed prior. The conclusion reached that states that it is a bad idea to pressurize nitrous oxide systems with nitrogen is applied by offering revisions in test firing procedures to reduce the time in which issues may occur. The conclusion reached that states that it is a good idea to pressurize nitrous oxide systems with nitrogen is applied by suggesting that no procedure or design changes should occur. Furthermore, this paper will serve as the precursor to experiments that will be conducted with nitrogen-nitrous oxide solutions using an 800lbf ethane-nitrous oxide rocket engine.

I. Nomenclature

P_{max} = maximum explosion pressure
$(dP/dt)_{max}$ = maximum pressure rise rate
CJ = Chapman-Jouguet detonation pressure
N = number of molecules that cross unit surface in unit time interval
C = concentration
D = mutual diffusion coefficient
w, a = some fluid
x = distance
$P_{1,2}$ = pressure of gas 1 or 2
ρ = gas mass density
A = pressure oscillation amplitude

II. Introduction

The fuel and oxidizer selections for a liquid bipropellant rocket are very diverse. However, there are many considerations when selecting propellant, such as environmental impact, danger, and cost of handling. In general, many student or amateur teams building a liquid bipropellant rocket have even more restrictions, as the high efficiency
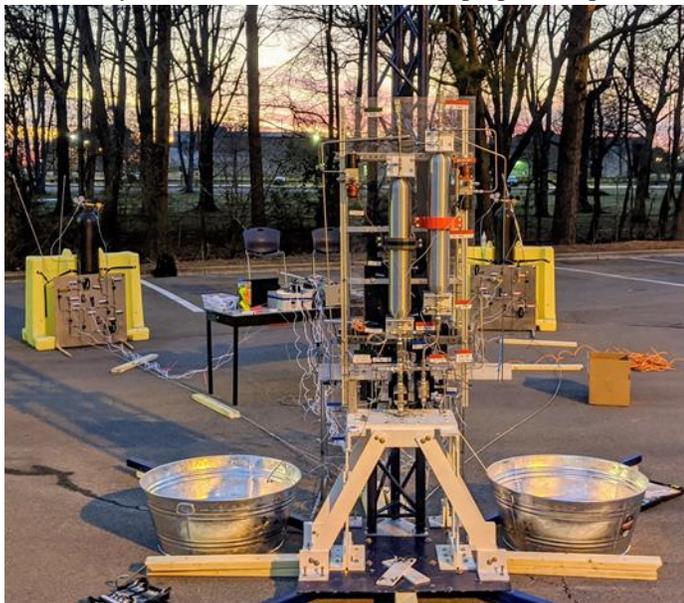
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hypergolic propellants preferred by professional rocketry companies are usually far too dangerous and expensive to handle. In addition, the use of turbopumps to pressurize the combustion chamber is also inadvisable for student/amateur teams due to lack of machining capabilities and funds. Therefore, the most popular choices of students/amateurs to pressurize their combustion chamber are usually self-pressurizing propellants like ethane or pressurization with an inert gas like nitrogen, which results in a blowdown pressure fed or a pressure-fed cycle, respectively. Given the fact that many professional rocketry firms do not use most of the propellants preferred by

amateurs and students, there is usually a lack of public research on the preferred propellants. This can lead to issues when student and amateur teams have problems with a certain property of their propellant, and they do not have enough information to discern how to fix the problem.

The Space Hardware Club at the University of Alabama in Huntsville is developing an ethane-nitrous oxide rocket engine under Project Tartarus. The objective is to execute a static firing test of an 800 lbf ethane-nitrous oxide engine in the spring 2020 semester. This introduces the possibility that mixing nitrogen in nitrous oxide will cause sub-par combustion or even combustion instabilities. If the solubility or diffusion rate of nitrogen in nitrous oxide is high enough, even a quick burst of nitrogen right into the tanks before the engine fires may be enough to induce unfavorable combustion during flight. This might cause a

Figure 1. Tartarus Test Stand as of Feb. 22, 2020

costly redesign of the rocket. Such a setback would sentence the project to another year or more of engine development. To avoid a major setback, the Tartarus team is investigating concerns about pressurizing nitrous oxide flight tanks with nitrogen.

Shown in Fig. (1) is the Tartarus static firing setup. The ignition process within the combustion chamber relies on nitrous oxide decomposing and then mixing with ethane to produce combustion. This is where the problems could begin if the tanks are pressurized with nitrogen. The vapor pressure of nitrous oxide at room temperature (20 ℃) is ~747 psi. Expectations are that the pressure of nitrogen entering the tank will reach or exceed 800 psi. Given that the nitrogen will be in a supercritical state when it enters the tank, there is a possibility that it could dissolve in the nitrous oxide. If this happens, there is a distinct possibility that the nitrous oxide will not decompose, and combustion will not occur. In addition, if only a small quantity of nitrogen dissolves in the nitrous oxide, then the nitrous oxide may still decompose but combustion instabilities may manifest. All these problems individually can jeopardize the static firing operation, but they could also compound and create an even more dangerous situation.

This paper is organized as follows: Section III discusses the mixing mechanics of nitrogen and nitrous oxide. The concept of combustion instability is presented in Section IV. In section V, the decomposition threshold of nitrous oxide and various nitrous oxide mixtures are evaluated. Finally, the paper is concluded with an analysis and conclusion statement in section VI, then a discussion of future research in section VII.

III. Mixing Mechanics of Nitrogen and Nitrous Oxide

In this section, the evaluation of the mixture of gaseous nitrogen and gaseous nitrous oxide will occur without consideration of supercriticality, liquid nitrous oxide, or gravity. Supercriticality of nitrogen and the presence of liquid nitrous oxide are unconsidered factors because there is no research on the interactions between supercritical nitrogen and liquid nitrous oxide. Modeling the interactions of the two fluids is very complex without conducting experiments. In the Tartarus system where nitrogen will flow into a tank full of nitrous oxide, the propellant will be flowing out of the tank so quickly that the mixing of the gases will be near negligible while the engine is firing. However, this is not the case in the instant before the engine fires, especially if the time between adding the nitrogen to the tank and firing the engine is greater than thirty seconds. Thus, an equation is needed to model the no longer negligible mixture of the two gases within the tank. The diffusion of two gases can be described by the Fick equation [1]:

$$N_w = D_{wa} \frac{dC_w}{dx} \quad N_a = D_{aw} \frac{dC_a}{dx} \tag{1}$$

Equation (1) models the diffusion of two gases by using the mutual diffusion coefficient (D) of fluids w and a, which can only accurately be calculated by experiment [1]. The Chapman-Enskog theory calculates the approximate value of the diffusion coefficient, but only to an accuracy of 8%, and the equation is not a function of pressure [2]. Realistically, the nitrogen and the nitrous oxide will be at very different pressures but similar temperatures. There will be a gradient of both temperature and pressure within both fluids. In the future, experiments will be conducted to determine the mutual diffusion coefficient. If the mutual diffusion coefficient of nitrogen and nitrous oxide is calculated, then Eq. (1) can be used to somewhat accurately determine the rate at which the gases will mix. Again, because the nitrous oxide is not yet flowing out of the tank, then the mixing process can be considered an isothermal process with the nitrogen and nitrous oxide at very similar temperatures. Equation (2) has been suggested to model the diffusion coefficient of two gases at different pressures and identical temperatures [2]:

$$\frac{D_{P_2}}{D_{P_1}} = \frac{\rho_{P_1}}{\rho_{P_2}} \tag{2}$$

An accurate estimate for the mixing rate of nitrogen and nitrous oxide at any pressure can be found by using Eq. (2) and the experimental value of the mutual diffusion coefficient [2]. Once this rate is determined, computer software can generate models of the approximate molar ratios of nitrogen to nitrous oxide at every point in the tank. Furthermore, once the effect of nitrogen on nitrous oxide decomposition is analyzed, then the molar ratios can be used to predict how much the nitrogen will affect combustion and decomposition processes. The molar ratios can also be used to predict how much nitrogen will be entering the combustion chamber at any time, which in turn enables the prediction of combustion instabilities.

IV. Combustion Instabilities

Using a pressure-fed cycle to push fuel and oxidizer out of their tanks is a very affordable and lightweight solution to make use of the propellants. However, there is no guarantee that the nitrous oxide will reach the combustion chamber without mixing with the inert nitrogen gas, even if the nitrogen is at a higher pressure. Therefore, there must be consideration of the effects of the nitrogen gas and how it could affect the combustion process.

A combustion instability, also known as a dynamic instability, is likely to occur when factors such as velocity, heat release, fuel/air ratio, or oscillation of pressure are changing within the combustion chamber at undesirable rates [3]. These instabilities can occur upon stimulation of acoustic nodes within the combustion chamber and typically lead to high-amplitude oscillations of pressure and velocity. When the flame is not held relatively steady and is instead allowed to sway side to side as one does during a combustion instability, the chances of the walls of the chamber undergoing heat stress greatly increase, especially in areas of smaller diameter such as the throat of the nozzle [3].

Figure 2. Driving/Damping Force vs Amplitude [3]

Although acoustic oscillations will most likely not affect the Tartarus engine due to its high modal frequencies, a possibility that combustion instabilities may propagate still exists. The acoustic oscillations within a combustion chamber cause the system to experience a continuous loop of issues. The acoustic nodes which induce changes in velocity and pressure within a chamber cause the rate of heat release to oscillate. The changing rate of heat release further encourages the acoustic oscillations to grow, which initiates the changes in velocity and pressure and brings the system through a full loop. This cycle can occur in both directions either adding or removing energy from the acoustic field [3]. Due to the cycle, the change in energy becomes dependent on the amplitude, which means instability will continue to increase until the system fails. It is important to note that the amplitude of the instability will only increase if the rate of addition of energy to the system is greater than the rate at which damping processes remove energy from the system [3].
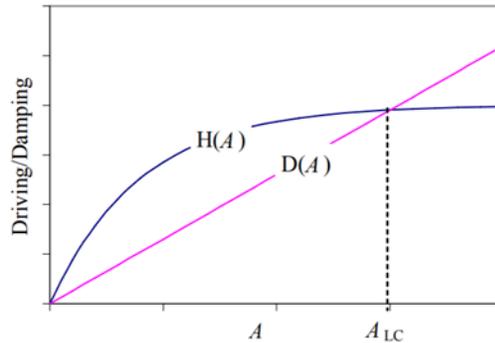
In a linear unstable system even the smallest difference of pressure will result in the continuous growth of the amplitude instability, which leads to an oscillation cycle [3]. Figure (2) represents a system in which the driving force, $H(A)$, is not linear. The driving force adds energy to the system. The linear damping force $D(A)$ removes energy from the system. Both forces are functions of the amplitude, A, of the system. As Fig. (2) shows, there are two intersections between $H(A)$ and $D(A)$. The first occurs at amplitude $A = 0$ where no driving or damping forces exist. This represents an equilibrium, but any disturbance to the system would lead to a divergent event in which $H(A)$ and $D(A)$ grow further apart as the amplitude increases. The second intersection represents a certain limit cycle amplitude, A_{LC}, at which $H(A)$ and $D(A)$ intersect. This is an equilibrium point of the system.

In a nonlinear unstable system, there is a region where the system can absorb smaller disturbances and still return to its equilibrium state [3]. This means if the disturbances caused by factors such as pockets of pressure change do not exceed a certain value, the system will function normally. Figure (3) represents this event. If amplitude A is less than A_T, the damping and driving forces will decay to the equilibrium point at $A = 0$. This applies to our Tartarus system because the utilization of nitrogen gas to force the nitrous oxide out of the tank could easily create pockets of pressure differences within the mixture before reaching the combustion chamber. If the pockets of pressure differences exceed a certain experimentally found threshold, A_T, then the instability amplitude will increase until system failure. If the pockets of pressure

Figure 3. Driving/Damping Force vs Amplitude [3]

differences do not exceed that threshold, then the system will be able to return to equilibrium without issue. Careful design and operation of combustion experiments should reduce the chance of unforeseen combustion instabilities. This behavior is directly related to our interest because the mixture rate of nitrogen and nitrous oxide directly influences the concentration of nitrogen at certain spaces within the combustion chamber.
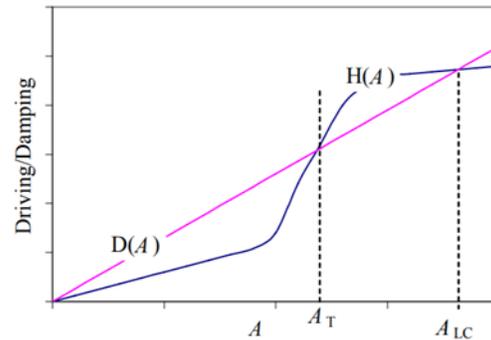
V. Effect of Added Nitrogen on Nitrous Oxide Decomposition

Reference [4] contains the experimental data from a series of tests conducted by Juris O. Krisjanons, Loren E. Bollinger, and Rudolph Edse at Aerospace Research Labs. Their experiments determined the explosive limits of nitrous oxide and nitrous oxide-nitrogen-air mixtures over a high range of temperatures and pressures. The experimental setup was designed to accurately measure the change in pressure within the vessel to determine whether partial decomposition or an explosion occurred. These experiments help model what happens to the decomposition threshold of nitrous oxide when nitrogen and nitrous oxide interact. Reference [5] describes experiments using ethylene-nitrous oxide mixtures diluted with nitrogen or carbon dioxide. The goal of the study was to determine the explosion pressure limits of nitrous oxide with an initial temperature of 298 K and at varying pressures when it is mixed with ethylene and diluted with varying percentages of nitrogen or carbon dioxide. In the context of a rocket engine, these experiments help quantify what would happen to the decomposition threshold of nitrous oxide if the fluid mixes with nitrogen and then becomes contaminated with a small amount of hydrocarbon. The experiments from reference [5] occurred in a standard 20 L pressure vessel using a 10 J electric shock to excite the nitrous oxide.

A. Decomposition of Pure Nitrous Oxide

Chemically, the most difficult part of building a bipropellant rocket engine with nitrous oxide as one of the propellants is getting the nitrous oxide to decompose before interacting with the fuel. Nitrous oxide is difficult to decompose in a natural setting, but when exposed to pressures above 20 atm and temperatures above 400 °C it decomposes readily as demonstrated by Fig. (4) (Ref. [4]). The propagation of nitrous oxide decomposition will not be that difficult to achieve inside or on the way to the combustion chamber because the vapor pressure of nitrous oxide alone at 20 °C is around 50.83 atm, meaning that the gas will easily decompose at around 180 °C [4].
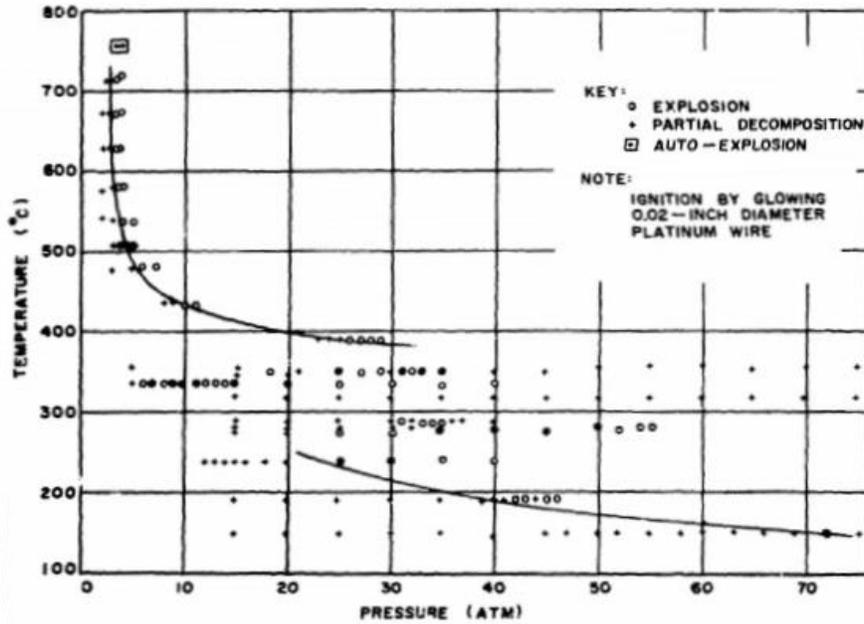
Figure 4. Measured Explosion Limits of Nitrous Oxide [4]

B. Decomposition of Nitrous Oxide-Nitrogen Mixtures

Using the same experimental methods, nitrogen was mixed with nitrous oxide and it was observed that, "No explosion or reactions of any kind were observed in the $N_2O + 0.88N_2$ mixture," [4]. In an identical temperature and pressure range as Fig. (4), the nitrous oxide would not even partially decompose when mixed with 0.88 moles of nitrogen. Using this data, it can be inferred that nitrogen is a very strong decomposition inhibitor, so presumably if nitrogen were to mix with nitrous oxide at an above negligible molar ratio then the required energy for nitrous oxide to decompose could be raised above attainable levels. If this is the case, then the nitrous oxide will not decompose. There will be no free oxygen in the combustion chamber for fuel to react with and no combustion will occur. If this were to happen during a test or even a launch, then a lack of thrust could compromise the entire operation. In the future, it will be very important to calculate the approximate molar ratio of nitrous oxide to nitrogen to prevent sub-optimal decomposition.

C. Decomposition of Nitrous Oxide-Hydrocarbon Mixtures with Nitrogen Dilution

Using the experimental methods described in reference [5], a nitrogen-nitrous oxide-ethylene mixture was ignited. From the experimental data, the results reached above were corroborated, "With the increase of N_2 or CO_2 addition, both P_{max} and $(dP/dt)_{max}$ decline gradually due to the decrease in the energy content of the mixture and the flame temperature by inert gas effect," [5]. The experiment found that with an equimolar mixture of nitrous oxide and ethylene allowed to mix for ten minutes the explosion energy was greater than nitrous oxide alone, which would not even decompose at the same temperature and pressure [4][5]. Therefore, it is reasonable to infer that any small hydrocarbon like methane or ethane would also lower the activation energy of nitrous oxide decomposition as well as react with the free oxygen formed from even partial decomposition. As opposed to nitrous oxide alone, an actual explosion would occur where the free oxygen formed by nitrous oxide decomposition would react with whatever contaminant entered it to produce flame. This in turn would cause runaway decomposition of the nitrous oxide. This property of a nitrous oxide-hydrocarbon mixture can cause major problems if some nitrous oxide undergoes exposure to contaminants, such as oils within pipes, on the way to the combustion chamber. Therefore, it is incredibly important to fully cleanse pipes that propellants, especially oxidizers, must travel through. Next, the experiment analyzed the effect of different percentages of nitrogen diluting the ethylene-nitrous oxide mixture as shown in Fig. 5 (Ref. [5]). As the figure shows, the less nitrogen added means the explosion pressure was higher. Compared to the data from reference [4], the nitrous oxide was able to at least partially decompose when mixed with nitrogen due to the presence of ethylene. If any fuel or general contaminants enter the nitrous oxide lines, then an explosion causing runaway nitrous oxide decomposition can occur regardless of the presence of nitrogen. In spite of the data from reference [4] showing that nitrogen is a very strong inhibitor for nitrous oxide decomposition, if the nitrous oxide tank or tubes the

nitrous oxide must travel through are contaminated then an explosion is still highly likely before the gas even reaches the combustion chamber [5].
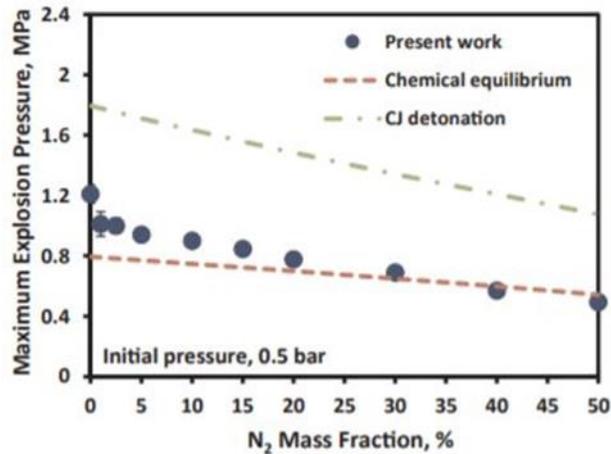

Figure 5. Maximum Explosion Pressure of a Nitrous Oxide-Ethylene-Nitrogen Mixture [5]

VI.   Conclusion

In this paper, combustive experiments performed with nitrogen-nitrous oxide mixtures were reviewed. Potential effects on bipropellant combustion were presented when mixing nitrogen in nitrous oxide. By evaluating the experimental data [4-5], as well as discussions in each section, the following conclusions can be drawn:

- The rate at which nitrogen and nitrous oxide mix is incredibly important for every issue outlined in this paper.
- Combustion instabilities are unlikely to occur, but nitrogen interrupting the fuel to oxidizer ratios within the combustion chamber does increase the odds of instabilities occurring.
- Regarding the decomposition threshold of nitrous oxide, nitrogen raises the threshold, while hydrocarbons lower it and allow for a runaway decomposition to occur.

The method for calculating the rate at which nitrogen and nitrous oxide will mix was discussed. Using the calculations with Eqs. (1) and (2) yields the molar ratios of nitrogen to nitrous oxide, which then determines the magnitude of their effect on the decomposition threshold of nitrous oxide. In addition, the molar ratios calculated can be used to predict potential combustion instabilities. Thus, the conclusion on whether it is advisable to pressurize a nitrous oxide tank with nitrous oxide becomes entirely dependent on how long the nitrogen is interacting with the nitrous oxide in the tank, the mutual diffusion coefficient (D) of nitrogen and nitrous oxide, and the critical pressure oscillation amplitude (A_T) within the engine. If the nitrogen is allowed to interact with the nitrous oxide within the tank for a significant period of time before the propellant is flushed, the mutual diffusion coefficient is high enough, and the critical pressure oscillation amplitude (A_T) is low enough, then it is a very poor choice to pressurize a tank of nitrous oxide with nitrogen. Given this scenario, the nitrogen will influence the decomposition threshold of the nitrous oxide enough to either cause a moderate to severe lack of thrust or inhibit combustion entirely. In addition, if combustion does occur, there is a distinct possibility that combustion instability will also occur due to the presence of the inert nitrogen and a low critical pressure oscillation amplitude. On the other hand, an ideal case would be where the nitrogen only sits in the tank with the nitrous oxide for a few seconds before the propellant drains, the mutual diffusion coefficient of nitrogen and nitrous oxide is low, and the critical pressure oscillation amplitude (A_T) is high. In this case, it is advisable to pressurize a nitrous oxide tank with nitrogen because the effect of the nitrogen will be negligible. The nitrogen will only slightly affect the threshold of nitrous oxide decomposition, so combustion will still occur nominally with only a very small loss of thrust. Moreover, combustion instability will also be negligible due to the low concentration of nitrogen within the combustion system. While conditional, the conclusion reached within this paper suffices to answer the question of pressurizing a tank of nitrous oxide with nitrogen if there are future experiments to obtain missing data. In terms of the Tartarus project, the ideal way to apply this conclusion will be to leave only a small amount of time between filling the tank with nitrogen and firing the engine. Currently, the setup the project has devised has a very long interval between steps like opening valves or reading pressure, so a revision in

the firing procedure will be needed to guarantee that the nitrogen pressurizing the nitrous oxide tank will not cause the issues discussed in this paper.

VII. Future Research

For the conclusion reached by this paper to become helpful for the Tartarus project which spawned it, future research is essential. The Tartarus team plans to conduct tests that enable the discovery of the mutual diffusion coefficient of nitrogen and nitrous oxide at a relevant temperature in conditions physically identical to the environment of the final Tartarus rocket. Once this test is conducted, further experiments will be set up, using the future Tartarus static firing rig. A fixed amount of nitrogen will be added to the nitrous oxide tank while varying the time the nitrogen spends sitting in the nitrous oxide tank before firing the engine. Finding the molar ratio which the nitrogen-nitrous oxide mixture cannot exceed in order to avoid combustion instabilities by way of inconsistent fuel/oxidizer mixture ratios will also utilize the same setup. Hopefully, these experiments will lead to a definitive answer to the questions posed by this paper.

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