STUDY OF HYPERGOLIC PROPELLANTS USING MICRO-REACTORS
Pulkit Saksena1*, Srinivas Tadigadapa2, Richard A. Yetter1
1Department of Mechanical and Nuclear Engineering, 2Department of Electrical Engineering
The Pennsylvania State University, University Park, PA, USA

ABSTRACT
This paper discusses a novel method to study hypergolic propellants using micro-reactors instead of the conventional drop test, modified version thereof or impinging jets. A new micro-reactor has been fabricated and tested to allow the study of hypergolic propellants which tend to be toxic and corrosive and thus a challenge for micro-fluidics.

KEYWORDS: Hypergolic Propellants, Micro-Reactors.

INTRODUCTION
Hypergolic bipropellants are defined as fuel and oxidizer pairs which are able to spontaneously ignite when they come in contact with each other. This spontaneous ignition negates the employment of a complex ignition system but the ignition does involve a complex interrelation between physical and chemical phenomena which is currently poorly understood. There has been widespread research on hypergolic propellants especially since the 1950s due to the fact that they have high density, long term storage ability and high performance. However as these fuels are usually very toxic and in some cases carcinogenic, there is a need to identify less toxic fuels. To develop these new fuels, we need a better understanding of the kinetic mechanisms taking place during hypergolic combustion.

Study of hypergolic fuels is usually done by either drop tests [1], mixing tests (in which the mixing between the reactants is increased) [2] or by impinging jets [3] (in which separate fuel and oxidizer injectors are used to enhance mixing and recreate typical rocket conditions). Although a large number of tests have been performed using setups similar to the drop test, the results can be affected by numerous variabilities in the experiment such as droplet size, droplet impact and mixing of the droplet with the other reactant. In our study we have chosen to use micro-reactors to study the interaction between the fuel and the oxidizer of hypergolic reactants, specifically emphasizing the liquid-phase reaction at the point (or instant) of contact. The advantage of micro-fluidic systems lies in their capability to utilize minute quantities of reagents to carry out reactions and analysis with high resolution in a time and cost-efficient manner. Moreover, unlike the case of macroscopic laboratory equipment, fluid behavior in micro-scale flow is dominated by non-convective, laminar flow, wherein diffusion alone is responsible for mixing, and thus the chemistry can be better isolated from the fluid mechanics.

The most popular fuel-oxidizer combination for hypergolic combustion has been monomethylhydrazine (MMH) with red fuming nitric acid (RFNA) due to their short ignition times and high specific impulse. Owing to the carcinogenic nature of MMH, an alternative fuel is sought and an intended replacement is tetramethylethylenediamine (TMEDA) [4]. Although the performance of TMEDA is not expected to surpass that of MMH, it has been shown to be less toxic [5]. Apart from simple data on ignition delay and specific impulse, no experimental studies have been conducted to study the hypergolic interaction between TMEDA and RFNA. This study aims at looking at hypergolic reagents in a new manner.

FABRICATION OF MICRO-REACTORS
Micro-fluidic channels are usually fabricated from poly di-methyl silioxane (PDMS) as they are relatively easy to batch process using the standard soft lithography and mold replica technique [6]. These channels give easy optical access and are relatively robust enough for most micro-fluidic studies. But due to the corrosive nature of the reagents under study, silicon based channels capped off with Pyrex were chosen instead of the usual PDMS. The use of silicon is also open to the questions of material compatibility between it and the various propellants. But coating the silicon substrates with an appropriate coating of either silicon nitride or another suitable metal may be easily carried out to avoid the material compatibility issue with silicon. It should be noted that there was no noticeable change in the surface of the reactors with the reagents used in the study and neither was there any surface reaction noticed.

In the case of the PDMS channels the inlet tubing is introduced into the channels by vertical holes into the polymer itself via conventional machining. Micro-machining of silicon is difficult and therefore the micro-reactor was designed to sit on a manifold where it would be held in place with a compression seal with inlet and the exhaust ports being etched into the silicon from underneath.

To etch both sides of the silicon, double side polished wafers were used and photolithography was carried out using the Micro-Chem KMPR, an i-line high contrast epoxy based photoresist, as it is able to provide a high etch selectivity as well as relatively higher thickness than other commonly used photoresists (1810 and 1827). The silicon wafer was then etched using
a deep reactive ion etching (DRIE) process where it was etched anisotropically using a modified Bosch process. The same process was repeated for etching the inlet and exhaust through-holes on the back-side of the wafer. After etching the wafer, the silicon wafer was bonded to a Pyrex wafer using anodic bonding and then diced into individual reactors.

Two sets of micro-reactors were fabricated for the study (Figure 1), with one mimicking the impinging jets experiment used widely to test hypergolic propellants while the other provided a stagnation flow within the channel. Each of the reactors had a main-channel with a width of 240µm, a total length of 1cm and a depth of 55–60µm. The width of the inlets for the reactors was varied between 120µm and 240µm to study various strain rates in the main channel.

EXPERIMENT

Manifolds (Figure 2) were fabricated for both sets of micro-reactors using SS 316. These manifolds helped in both providing a suitable way to pump the propellants into the reactors without causing too much of a pressure drop as well as providing a safe and secure way of collecting the exhaust fumes and residual salt. The inlets and outlets of the manifold to the reactor were sealed using Kalrez o-rings to prevent any leakage of the chemicals.

The experimental setup consisted of the manifold, with the reactor mounted, placed under an upright microscope (Nikon Eclipse LV100). A high speed camera (Phantom V 7.3) was mounted onto the upright microscope to optically study the flow in the micro-reactors. A pressure driven flow was used to create the fluid-flow in the micro-reactors with a positive pressure being applied at the inlets while keeping the exhaust open to atmospheric pressure. The fuel and oxidizer were introduced into the manifold using Teflon tubing connected to high pressure stainless steel syringes. These syringes were controlled by a high pressure syringe pump (Harvard Apparatus PHD4400), giving a high degree of control on the flow rates. Fine-wire shielded thermocouples were introduced into the exhaust reservoir of the channels to record the temperature of the exhaust fluids from the reactor. A rise in temperature at the exit was an indication that an exothermic reaction had occurred inside the reactor. A water trap and high velocity exhaust fan were also attached to the exhaust of the manifold for the safe disposal of the toxic products of the reaction. Experimental runs were made using TMEDA as the fuel and RFNA as the oxidizer. The oxidizer was diluted using di-methyl sulfoxide (DMSO) and distilled water, thus reducing the mass fraction of RFNA in the system, to provide a range of conditions in the test cell.

RESULTS AND DISCUSSION

Before running actual reagents through the reactors, cold-flow studies were performed to characterize the reactor. Perfectly laminar flow was achieved using the reactor and it was visualized, along with a clean interface by using just water at both inlets with micro-spheres added to once side while keeping the other inlet clear of all particles. The reactors were tested using three flow rates such that the Reynolds number of the flow in the channels were 14, 28 and 56. These flow rates yielded a residence time of about 2ms, 1ms and 0.5 ms per channel width respectively. There was a rise in the exit temperature of the reagents upon increasing the flow rates within the reactor. This could be linked to the fact that there was better mixing between the reactants by the time they reached the end of the channel thus giving rise to more reaction. It was noticed that diluting the oxidizer concentration resulted in a drop in the temperature of the products at the exit. This is mostly because of the lowering in the reaction rates between the reactants and also due to the lowering of the mass diffusion across the interface. Also noted with the introduction of DMSO was a shift of the interface between the reactants towards the side which had TMEDA flowing through. A more interesting observation was that there was a marked shift in the interface when dilution levels of the RFNA in the system were changed by adding DMSO. The interface shifted away from the RFNA inlet as the dilution of the RFNA entering the reactor was increased (Figure 3). This shift cannot be explained as a change in momentum flux between the two inlet fluids, as the shift is too large for the corresponding change in densities. More importantly the change is in the opposite direction expected by the change in momentum flux balance from the inlets or the fact that it was a shift due to the reaction just between TMEDA and RFNA.
To help understand this aberration, a set of experiments were also conducted using water to dilute the RFNA in similar proportions to the dilutions with DMSO. In this case there was very little movement of the interface while changing the dilution conditions in the reactor. Thus the changes in the RFNA-TMEDA system when diluted with DMSO may be explained by the fact that the system started behaving like a pre-mixed reaction supported by heat release from the diffusion controlled reaction between TMEDA and RFNA. A pure diffusion based reaction is supported by the stoichiometric, counterdiffusion of fuel and oxidizer and once initiated the reaction will situate itself between the fuel and oxidizer sources in order to satisfy the stoichiometric requirements. In a premixed system, the reaction front tends to propagate into and consume the unreacted mixture [7]. This is what appears to be occurring in the system when the RFNA is diluted with DMSO as the reaction front tends to travel towards the RFNA inlets.

CONCLUSION
A new novel micro-reactor has been fabricated for testing reactions between extremely corrosive reagents. Very steady reactions were observed in the micro-reactors with hardly a perturbation of the interface between the reactants. This bodes well for further study of the propellants using these micro-reactors as an excellent laminar flow has been established in the reactors, even with the reactions taking place at the interface.

ACKNOWLEDGEMENTS:
This material is based upon work supported by the U.S. Army Research Office under grant number W911NF-08-1-0124.

REFERENCES

CONTACT
*Pulkit Saksena, pzs124@psu.edu*