

8th U. S. National Combustion Meeting
Organized by the Western States Section of the Combustion Institute
and hosted by the University of Utah
May 19-22, 2013

The Effects of Nano-Scale Additives on the Linear Burning Rate of Nitromethane at High Pressure

Kenneth W. McCown III Eric L. Petersen

Mechanical Engineering, Texas A&M University, College Station, Texas, 77843, USA

This paper examines the effects of various nanoparticle additives on the combustion behavior of nitromethane, using an alternate method recently developed by the authors to measure the linear burning rates of liquid monopropellants. Nano-scale aluminum (100 nm diameter) was used to increase the overall energy density of the mixture, and fumed silica powder (200 to 300 nm aggregate) was used to increase the mixture thickness and encourage aluminum suspension. Nano-scale titania (20 nm diameter) was also included as a useful additive, based on previous studies that showed marked increases in the burning rates of solid monopropellants with added titania. The effects of these added particles on linear burning rates were tested at chamber pressures ranging from 3 to 13 MPa, using a technique that functioned without direct observation of the burning front progression. The added amount of fumed silica powder was varied from 1% to 3% by mass, aluminum was varied from 5% to 13.5% by mass, and titania was added at 1% by mass for all relevant trials. The mass percentage of suspended aluminum was limited by the viscosities of the resulting mixtures and represented the maximum amounts that still allowed the mixture to flow as a liquid. The use of fumed silica powder yielded increased linear burning rates compared to neat nitromethane, and the pressure exponent of the burning rate equation shifted from lower to higher than neat nitromethane as more silica was added to the mixture. The addition of aluminum to this silica mixture led to further increases in linear burning rates, and the exponential factors consistently showed increased pressure sensitivities for those mixtures containing aluminum. The combination of nano-scale titania and nitromethane led to higher linear burning rates with increased pressure sensitivity and combustion instability for chamber pressures above approximately 8 MPa, but decreased pressure sensitivity for the same mixture below 8 MPa. However, the addition of titania to mixtures already containing silica and aluminum slightly decreased their burning rates, reversing the accelerating effect seen in mixtures that contained only nitromethane and titania.

1. Introduction

Recent efforts within the aerospace industry have focused on replacing widely used hydrazine and hydrazine-based propellants with materials such as energetic ionic liquids (EILs) and other monopropellants (Edwards, 2003). While hydrazine is known to present a severe health risk to humans and the environment, EILs have been shown to possess reduced toxicity and other favorable characteristics that increase their ability to be handled and stored. Though not technically an EIL, nitromethane is a liquid monopropellant whose physical properties are well suited for controlled laboratory study. Its low cost, widespread production, low toxicity, ease of storage, high energy density, and high specific impulse when compared to currently used hydrazine propellants make nitromethane a useful surrogate for the development of liquid monopropellant testing methods that will later be applied to a wide range of EILs. The addition of nano-scale metal and metal oxide additives to EILs and nitromethane allows the burning rate to be altered to better match the requirements of specific propulsion applications while simultaneously contributing to the specific impulse of the propellant. The relative stability and safety of nitromethane allow researchers to concentrate solely on the tailoring of combustion behavior through these additives, uncovering performance trends that will guide future studies completed with more exotic EILs.

The combustion behavior of liquid monopropellants, including nitromethane, have been extensively studied by past groups, yielding a large variety of monopropellant ignition techniques that range from resonant lasers (Alfano, 2009) to heated nickel-chromium wire (Kuo, 2000 and Smiglak, 2006). Beginning shortly after World War II, NAVORD conducted studies to determine the burning rate of nitromethane as a function of chamber pressure (Rice, 1953), while similar burning rate studies were conducted two decades later in Moscow (Raikova, 1977). After an additional two decades, researchers from Pennsylvania State University measured the temperature sensitivity and intrinsic burning rate

of nitromethane in a liquid-fed burner system (Boyer, 1997). Members from this same group also studied the burning rate of nitromethane under static strand burner conditions (Boyer, 1999) separately from researchers in Germany (Kelzenberg, 1999), while Boyer continued his work on measuring and modeling nitromethane combustion with a dissertation in 2005. The extensive range of chamber pressures used to test the burning rate of nitromethane stretched from 0.5 to 172 MPa, yet these previous studies acknowledged the presence of several different pressure regimes of burning behavior. Within each of these ranges, the burning rate of nitromethane (r) is defined using the same numerical form shown in Eq. (1), but with a different pre-exponential coefficient describing the effect of initial propellant temperature (a) and exponential factor describing the effect of chamber pressure (n) (Sutton, 2001).

$$r = aP^n \quad (1)$$

A particular pressure regime was found between 3 and 15 MPa and extensively tested (Boyer, 1999 and Boyer, 2005), so the pressure limits of the current study were set at similar values of 3 and 13 MPa to facilitate a direct comparison of mixture results to a well-established nitromethane baseline.

Nano-scale additives in liquid propellants have also been examined, ranging from synthesized alumina catalysts dissolved in JP-10 (Wickham, 2006) to various concentrations of aluminum powder mixed with water (Risha, 2007). However, the effects of nano-scale additives on the specific burning behavior of nitromethane have only recently entered the arena of study. One past report examined the behavior of nitromethane gelled by Aerosil 200 fumed silica and ALEX fine aluminum particles (Weiser, 2005). A separate study examined the effect of nano-scale, functionalized graphene sheets on the burning rate of nitromethane, measuring marked increases in the linear burning rate of mixed samples over neat nitromethane (Sabourin, Dabbs, 2009). The same group returned to testing nitromethane mixtures, this time with varying concentrations of 38- and 80-nm diameter aluminum and CAB-O-SIL TS-720 fumed silica that also showed measurable increases in linear burning rates for increasing additive concentrations (Sabourin, Yetter, 2009). Earlier this year, a previous study by the authors chronicled the development and implementation of a new technique to estimate the linear burning rate of both liquid monopropellants and heterogeneous mixtures without direct observation of the burning front (McCown, 2013). This study was built on the groundwork laid in a thesis that described initial attempts to measure the linear burning rate of plain nitromethane in a similar strand burner configuration (Warren, 2012).

The objective of the current study was to use this recently developed method to explore the effects of added nano-scale particles on the linear burning rate of nitromethane. Various concentrations of aluminum, silica, and titania nanoparticles were used to alter the combustion behavior of each mixture. Both the separate and combined effects of the additives were then compared to isolate the influence of each material on the temperature coefficient and pressure exponent of the propellant burning rate. This paper describes the use of the authors' alternate technique to study these additive effects, including measures taken to quantify particle settling and eliminate it from tested propellant mixtures. By including the effects of a wide variety of particle additives and respective mass concentrations, the paper confirms several previous observations made by other research groups and uncovers additional trends that encourage further study.

2. Methods

The nitromethane used in the current study was ACS reagent grade and purchased from Sigma-Aldrich Co. Nano-scale aluminum particles with a mean diameter of 100 nm and an average specific surface area of 10 to 20 m²/g were chosen as additives for nitromethane and purchased from US Research Nanomaterial, Inc. Other groups reported that similarly sized aluminum particles were difficult to suspend in nitromethane without the addition of a thickening agent, with silica powder serving as a common thickener of choice (Weiser, 2005 and Sabourin, Yetter, 2009). Fumed silica powder consisting of 200 to 300 nm aggregate particles with an average specific surface area of 200 m²/g was chosen as the thickening agent for the current study and purchased from Sigma-Aldrich Co. Titania particles with a mean diameter of 20 nm and an average specific surface area of 148 m²/g were purchased from Mach I, Inc. and chosen as the final additive for the current study. To determine the weight percentages of each constituent material, the nitromethane and dry powders were individually weighed using an Ohaus ARA520 digital scale with a resolution of 0.01 g. An excessive, 50 g of nitromethane were used as the base for each mixture, diminishing the relative error caused by limited scale resolution and decreasing the likelihood of sunken agglomerates being drawn up during sample extraction. It is useful to note that the reported aluminum weight percentages are inclusive of any oxide coating.

The strand burner system used in the current study recorded the instantaneous pressure, light intensity, and electromagnetic emission spectrum of a small sample of solid or liquid propellant throughout the combustion process. To measure combustion behavior over a wide range of ambient pressures, the strand burner was pressurized to the desired conditions using compressed air. The additional oxygen present in the air was only necessary to initialize burning in mixtures with low particle concentrations; the rapid movement of the flame front below the mouth of the cavity after ignition prevented further access to the ambient oxygen and forced each mixture to burn as a monopropellant for the

remainder of each test. A custom bolt insert was created to fit into the bottom of the strand burner and house the current mixture sample within a small cavity, as illustrated in Fig. 1. A nickel-chromium wire was passed across the top surface of the cavity and connected the two leads of an electrode embedded in the bolt, igniting the monopropellant through resistance heating of the wire. At lower initial pressures, some mixtures became increasingly difficult to ignite and necessitated the use of a small segment of mono-modal AP/HTPB solid rocket propellant threaded onto the wire. A fused quartz tube insert with an inner diameter of 7 mm was used in every trial to separate the loaded monopropellant from the carbon steel walls of the bolt cavity, minimizing any unquantifiable heat transfer or catalytic effects on the mixture.

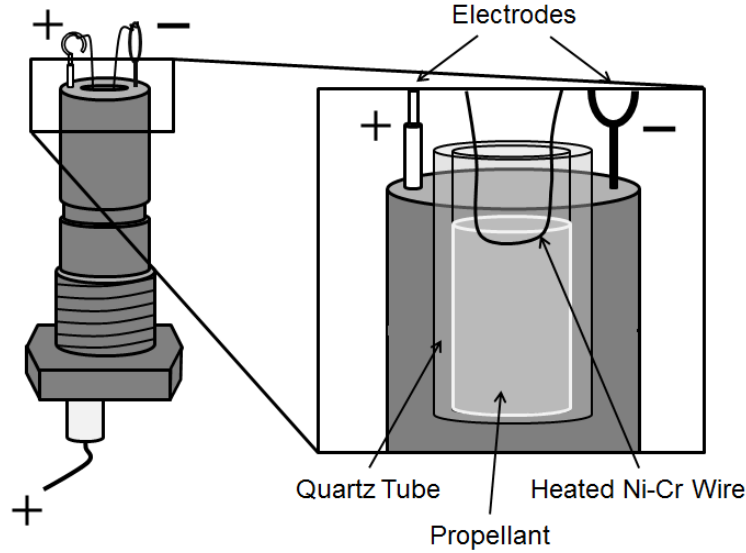


Figure 1: Custom bolt insert used to house and ignite liquid monopropellant in stand burner.

The linear burning rate (r) for each trial was defined for the current study by Eq. (2).

$$r = \frac{\Delta x}{\Delta t} = \frac{\left(\frac{m}{\rho}\right) / \left(\frac{\pi d^2}{4}\right)}{\Delta t} \quad (2)$$

where the burning time (Δt) was determined from the rise and fall of the recorded pressure trace, and the axial length of burned propellant (Δx) was calculated using the measured mass of propellant burned during each trial (m), the known propellant cavity diameter (d), and the known density of the monopropellant mixture (ρ). Spectroscopic emission data were also collected for each trial, allowing the authors to examine each combusted sample for signs of contaminants that could cause anomalous burning behavior. A more detailed description of the strand burner, custom bolt insert, data acquisition system, and pressure trace interpretation methods may be found in a previous study and thesis related to the current research (McCown, 2013 and Warren, 2012).

To ensure that the measured burning rates were not affected by particles that had agglomerated over time, propellant mixtures were combined and agitated just prior to testing. A Sper Scientific, Ltd. ultrasonic mixer was used to encourage even mixing at 42 kHz and prevent particle agglomeration for a full 25 minutes before each test, and a plastic pipette was used to load the mixture into the bolt cavity before insertion into the strand burner. Even without any widespread agglomerations, some particle mixtures were simply unable to remain suspended for enough time to be reliably tested. To guarantee that no tested mixtures would settle in the few minutes between loading and ignition, a settling study was completed to measure the longevity of each particle suspension and the mass percentage of particles that had not settled to the bottom of the mixture volume. After the ultrasonic mixing period, each mixture was agitated by hand and then left undisturbed for the remainder of the settling study. At various intervals of time, a large pipette was used to draw liquid from a depth slightly below the surface of the mixture volume. The same drawing depth was used for each subsequent time interval, and each liquid sample was deposited into separate glass beakers. The initial mass of each liquid sample was measured using the same Ohaus ARA520 digital scale, and the samples were allowed to dry overnight under ambient atmospheric conditions. The final mass of each dried sample was then compared to its respective initial mass, revealing the mass percentage of solid material that had originally been present.

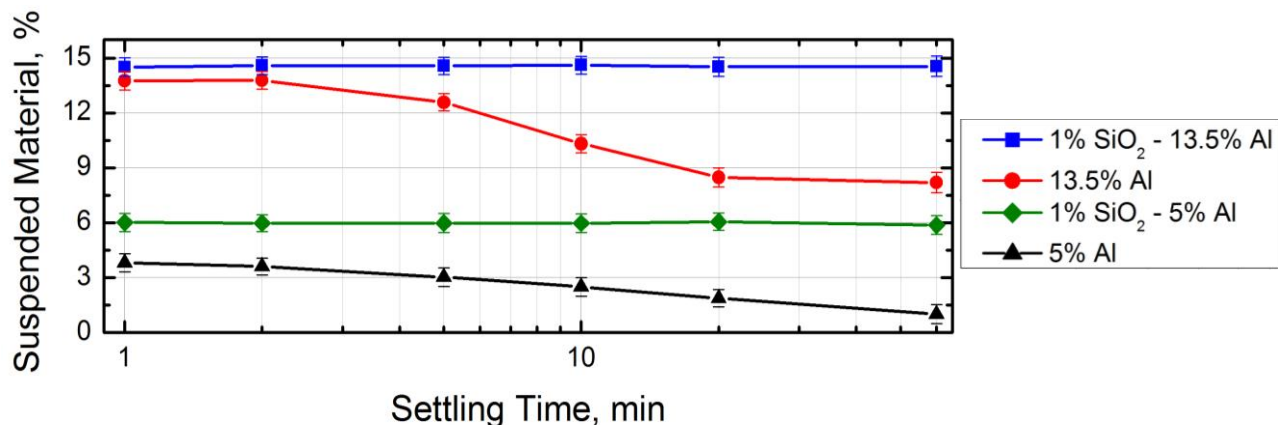


Figure 2: Mass percentages of suspended particles as functions of settling time for select mixtures.

Several settling curves representing both stable and unstable suspensions are provided in Fig. 2 to summarize the results of this study. The nearly horizontal curves of the mixtures containing both silica and aluminum indicated stable particle suspensions that could be reliably tested, while the decaying curves of the mixtures that contained only aluminum confirmed the reports of previous groups that concluded an additional thickening agent was required to ensure repeatable trials with larger-diameter aluminum particles (Weiser, 2005 and Sabourin, Yetter, 2009). While not exhaustively represented in Fig. 2, all tested mixtures were first determined to be stable in this manner before combustion testing in the strand burner took place.

3. Results and Discussion

Initial tests utilized a consistent 1% mass loading of fumed silica to better enable suspension of the aluminum nanoparticles, as discussed previously in the Methods section. To isolate the effects of this silica base from those caused by the subsequently added aluminum particles, a complete burning rate curve was created for a mixture containing only nitromethane and 1% silica by mass. This behavior was compared to the burning curves of two other mixtures containing and additional 5% and 13.5% mass loading of aluminum.

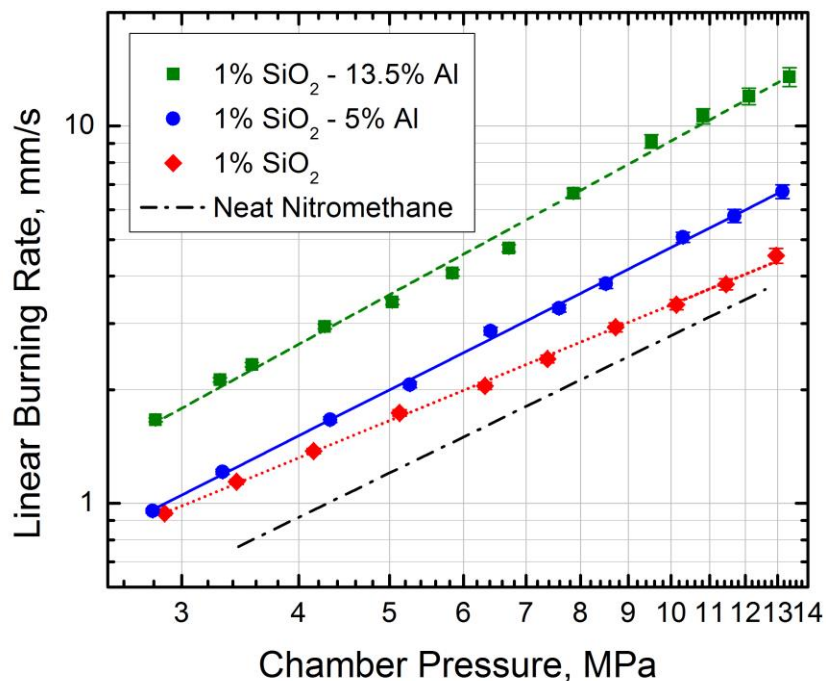


Figure 3: Linear burning rates of nitromethane mixtures containing 1% fumed silica.

The maximum 13.5% aluminum loading was set by the viscosity of the mixture, where more aluminum powder resulted in a thick, gel-like mixture that could not be easily loaded into the bolt cavity with a pipette. Figure 3 shows the measured trends for each of these mixtures and compares them to a previously established baseline curve for neat nitromethane (McCown, 2013). The added silica increased the linear burning rates over those of neat nitromethane for all tested pressures and increased the burning rate temperature coefficients. The most important effect of the 1% silica additive was a marked decrease in the burning rate pressure exponent, matching similar observations in a previous study where the decreased pressure sensitivity was attributed to possible catalysis or gas flame stabilization over solid particles present in the combustion products (Sabourin, Yetter, 2009). Conversely, the added aluminum increased the pressure sensitivity of each mixture as a function of higher aluminum loading; this trend also matched behavior seen in the same study (Sabourin, Yetter, 2009). The moderate 5% aluminum load appeared to decrease the temperature coefficient of its mixture, yet the larger 13.5% load reversed this trend with the increased temperature coefficient of its respective mixture.

To better understand the effects of silica on the combustion behavior of nitromethane and aluminum mixtures, a similar round of testing was completed with an increased silica loading of 3% by mass. This increased loading resulted in much greater mixture viscosities, severely limiting the amount of added aluminum to only 5%. Direct comparisons could still be made between these two mixture sets, because one of the previous mixtures had utilized the same 5% aluminum load. Figure 4 shows the measured trends for the two 3% silica mixtures and compares them to the previously cited nitromethane baseline.

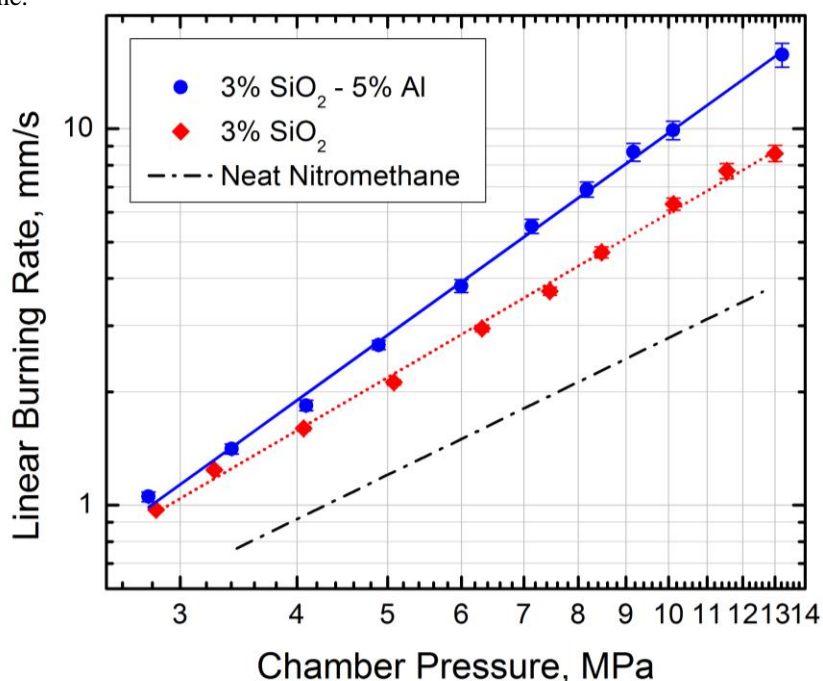


Figure 4: Linear burning rates of nitromethane mixtures containing 3% fumed silica.

As before, the added silica increased the linear burning rates and temperature coefficients over those of neat nitromethane for all tested pressures. However, the increased 3% silica loading actually increased the burning rate pressure exponent of both mixtures, indicating a higher pressure sensitivity previously unobserved by other studies. Interestingly, the presence of 2% greater silica actually increased the burning rates and pressure sensitivity of its mixture more than an entire 5% of added aluminum. In addition, the greater silica loading resulted in lower temperature coefficients than those seen for only 1% silica, affecting the mixture in much the same way as the aluminum presented in Fig. 3 and Fig. 4. For all tested mixtures, the added aluminum consistently decreased the temperature coefficients and increased the pressure exponents of their respective burning rate curves.

Collaboration between Texas A&M University and the University of Central Florida produced several studies that explored the use of nano-scale titania to alter the linear burning rates of solid propellants (Stephens, 2010 and Reid, 2011). In a similar fashion, the authors of the current study have begun to investigate the effects of titania on the combustion behavior of nitromethane. Figure 5 shows the resulting trends for mixtures containing 1% titania by mass and compares them to the same nitromethane baseline. For tested chamber pressures below approximately 8 MPa, the pressure exponent and temperature coefficient effects of 1% titania were similar to those of the added 1% silica

represented in Fig. 3. However, this behavior abruptly shifted as chamber pressures were increased above the 8-MPa threshold.

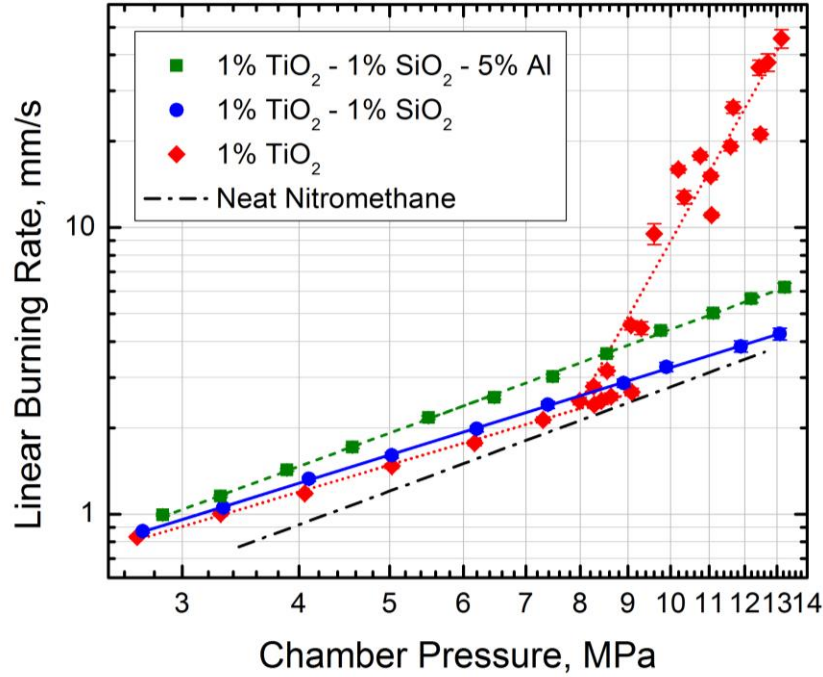


Figure 5: Linear burning rates of nitromethane mixtures containing 1% titania.

At these elevated pressures, the mixture containing only 1% titania experienced a drastic increase in the burning rate pressure exponent and an equally dramatic decrease in the temperature coefficient of its burning curve. This apparent inflection point resembled the shift between pressure regimes that was described in the Introduction and observed by groups that had previously studied the behavior of nitromethane over larger ranges of chamber pressures, albeit at a much reduced pressure. This shift in burning behavior above 8 MPa was also accompanied by increased combustion instability, as evidenced by the slightly elevated data scatter not found in any other tested mixture. Interestingly, the presence of 1% titania in mixtures that already contained silica actually decreased the linear burning rate by a small amount, and the negative impact remained even after the addition of 5% aluminum. This apparent reversal in the beneficial effects of titania and lack of drastic burning rate shifts for other titania mixtures may have indicated an attenuating interaction between silica and titania during combustion; this possibility could be explored through the testing of a greater variety of silica and titania mixtures in nitromethane. The final burning rate equation factors and statistical goodness-of-fit R^2 parameters of all tested configurations are compiled in Table 1 for review.

Table 1: Burning rate and R^2 parameters for tested monopropellant configurations.

Mixture	Temperature Coefficient (a)	Pressure Exponent (n)	R^2 Correlation
Neat Nitromethane	0.172	1.21	0.999
1% SiO ₂	0.321	1.02	0.999
1% SiO ₂ - 5% Al	0.266	1.25	0.999
1% SiO ₂ - 13.5% Al	0.404	1.35	0.994
3% SiO ₂	0.212	1.45	0.997
3% SiO ₂ - 5% Al	0.160	1.78	0.998
1% TiO ₂ (\leq 8 MPa)	0.313	0.967	0.998
1% TiO ₂ (\geq 8 MPa)	1.36×10^{-5}	5.82	0.936
1% TiO ₂ - 1% SiO ₂	0.314	1.01	1.000
1% TiO ₂ - 1% SiO ₂ - 5% Al	0.277	1.20	1.000

4. Conclusions

The varied effects of nano-scale aluminum, silica, and titania particles on the linear burning rate of nitromethane demonstrated the viability of using metal and metal-oxide additives to significantly alter the behavior of liquid monopropellants. While the current study only represented an initial foray into the arena of heterogeneous monopropellant combustion, the observed burning trends and extremely low data scatter validated the use of the authors' method to measure the combustion behavior of a wide variety of monopropellant and additive mixtures. The added aluminum particles consistently increased the pressure sensitivities of all relevant mixtures, but a separate increase in the temperature coefficient was limited to only the mixture containing 13.5% aluminum. Similarly, the added silica particles were capable of both increasing and decreasing the pressure sensitivities of mixtures depending on the silica concentration, with the 1% and 3% loads causing lower and higher pressure sensitivities, respectively. The opposing directions of these effects call for additional testing to identify why the same additive appears to have the opposite effect depending on its mass percentage. The dynamic increase in the burning rate of nitromethane and 1% titania at 8 MPa, coupled with the apparently negative impact of titania in the presence of other additives, also invites further testing to identify specific interactions between the three nano-scale additives used in this study. The authors hope to continue using their recently developed method to test other colloidal suspensions in nitromethane, as well as a greater variety of EILs and heterogeneous monopropellants.

References

- Alfano, A., Mills, J., and Vaghjiani, G., "Resonant Laser Ignition Study of HAN-HEHN Propellant Mixture," *Combustion Science and Technology*, Vol. 181, No. 6, 2009, pp. 902-913.
- Boyer, E., "Combustion Characteristics and Flame Structure of Nitromethane Liquid Monopropellant," Ph.D. Dissertation, Mechanical Engineering Dept., The Pennsylvania State University, University Park, PA, 2005.
- Boyer, E., Koch, D., Kuo, K. K., and Lu, Y. C., "Intrinsic Burning Rate and Temperature Sensitivity of Nitromethane," JANNAF Combustion Subcommittee Meeting, 34th, NASA 19980202209, 1997.
- Boyer, E. and Kuo, K. K., "High-pressure Combustion Behavior of Nitromethane," *AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit*, 35th, AIAA-99-2358, Los Angeles, CA, 1999.
- Edwards, T., "Liquid Fuels and Propellants for Aerospace Propulsion: 1903-2003," *Journal of Propulsion and Power*, Vol. 19, No. 6, 2003, pp. 1089-1107.
- Kelzenberg, S., Eisenreich, N., Eckl, W., and Weiser, V., "Modelling Nitromethane Combustion," *Propellants, Explosives, Pyrotechnics*, Vol. 24, No. 3, 1999, pp. 189-194.
- Kuo, K. K., Chang, Y. P., and Boyer, E., "Intrinsic Burning Behavior and Flame Structure Diagnostics of Liquid Propellants," U.S. Army Research Office, Rept. 20001124 014, PA, Jul. 2000.
- McCown, K. W., Warren, W. C., and Petersen, E. L., "Experimental Techniques to Study the Effects of Nano-Scale Additives on the Burning Rates of Liquid Monopropellants," *AIAA Aerospace Sciences Meeting*, 51st, Grapevine, TX, 2013.
- Raikova, V. M., "Limit Conditions of Combustion and Detonation of Nitroesters and Mixtures on their Base," Ph.D. Dissertation, Mendeleev Institute of Chemical Technology, Moscow, 1977.
- Reid, D. L., Kreitz, K. R., Stephens, M. A., King, J. E. S., Nachimuthu, P., Petersen, E. L., and Seal, S., "Development of Highly Active Titania-Based Nanoparticles for Energetic Materials," *Journal of Physical Chemistry C*, Vol. 115, No. 21, 2011, pp. 10412-10418.
- Rice, T. K. and Cole, J. B., Jr., "Liquid Monopropellants Burning Rate of Nitromethane," Naval Ordnance Lab Report NAVORD-2885, White Oak, MD, 1953.
- Risha, G. A., Son, S. F., Yetter, R. A., Yang, V., and Tappan, B. C., "Combustion of Nano-Aluminum and Liquid Water," *Proceedings of the Combustion Institute*, Vol. 31, No. 2, 2007, pp. 2029-2036.
- Sabourin, J. L., Dabbs, D. M., Yetter, R. A., Dryer, F. L., and Aksay, I. A., "Functionalized Graphene Sheet Colloids for Enhanced Fuel/Propellant Combustion," *ACS Nano*, Vol. 3, No. 12, 2009, pp. 3945-3954.
- Sabourin, J. L., Yetter, R. A., Asay, B. W., Lloyd, J. M., Sanders, V. E., Risha, G. A., and Son, S. F. "Effect of Nano-Aluminum and Fumed Silica Particles on Deflagration and Detonation of Nitromethane," *Propellants, Explosives, Pyrotechnics*, Vol. 34, No. 5, 2009, pp. 385-393.
- Smiglak, M., Reichert, W. M., Holbrey, J. D., Wilkes, J. S., Sun, L., Thrasher, J. S., Kirichenko, K., Singh, S., Katritzky, A. R. and Rogers, R. D., "Combustible Ionic Liquids by Design: Is Laboratory Safety Another Ionic Liquid Myth?" *Chemical Communications*, Vol. 24, May, 2006, pp. 2554-2556.
- Stephens, M. A., Petersen, E. L., Carro, R., Reid, D. L., and Seal, S., "Multi-Parameter Study of Nanoscale TiO₂ and CeO₂ Additives in Composite AP/HTPB Solid Propellants," *Propellants, Explosives, Pyrotechnics*, Vol. 35, No. 2, 2010, pp. 143-152.
- Sutton, G. P. and Biblarz, O., *Rocket Propulsion Elements*, 7th ed., John Wiley & Sons, New York, 2001.

- Warren, W. C., "Experimental Techniques for the Study of Liquid Monopropellant Combustion," Thesis, Mechanical Engineering Dept., Texas A&M University, College Station, TX, 2012.
- Weiser, V., Eisenreich, N., Kelzenberg, S., Plitzko, Y., and Roth, E., "Influence of ALEX and Other Aluminum Particles on Burning Behavior Gelled Nitromethane Propellants," *International Autumn Seminar on Propellants, Explosives, and Pyrotechnics (IASPEP 2005)*, Beijing, 2005.
- Wickham, D. T., Cook, R., De Voss, S., Engel, J. R., Nabity, J., "Soluble Nano-Catalysts for High Performance Fuels," *Journal of Russian Laser Research*, Vol. 27, No. 6, 2006, pp. 552-561.