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Effects of nano-scale additives on the linear burning rate of nitromethane

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This paper examines the effects of various nanoparticle additives on the combustion behavior of nitromethane, using a pressure-based method recently demonstrated by the authors to measure the linear burning rates of liquid monopropellants and heterogeneous mixtures with high precision. The linear burning rates of these mixtures were measured in a constant-volume system at chamber pressures ranging from 3 to 14 MPa, all without direct observation of the burning front. Nano-scale aluminum was used to increase the overall energy density of the mixture, fumed silica powder was used to increase the mixture thickness and encourage aluminum suspension, and nano-scale titania was also included based on its previous use as a burning rate modifier in solid propellants. The silica loading was varied from 1% to 3% by weight, aluminum was varied from 5% to 13.5% by weight, and titania was added at 1% by weight. The use of fumed silica yielded increased burning rates compared to those of neat nitromethane, and the pressure exponent of the burning rate curve shifted from lower to higher than the nitromethane baseline as more silica was added. This increased pressure sensitivity for mixtures containing 3% silica by weight was previously unobserved in similar studies by other groups and may be an effect of the higher specific surface area of the currently used silica. The subsequent addition of aluminum led to even faster burning rates and higher pressure exponents for all but one mixture. The addition of titania also led to elevated burning rates, with dramatically increased pressure sensitivity and rate inconsistency for chamber pressures above approximately 8 MPa but a decreased pressure sensitivity for the same mixture below 8 MPa. These changes in combustion behavior that accompanied titania were diminished by the presence of aluminum and completely negated in mixtures also containing fumed silica.

1. Introduction

For many years, hydrazine has been utilized as the primary monopropellant in a wide variety of aerospace applications, ranging from the first stage of the Titan II to the cruise stage of the recently launched Mars Science Laboratory. Within the last two decades, the severe health and environmental risks posed by toxic hydrazine and hydrazine-based compounds have renewed interest in alternative monopropellants. In the wake of this search, energetic ionic liquids (EILs), peroxides, and other monopropellants have emerged as possible replacements for hydrazine [1]. The low vapor pressures, reduced toxicities, and high thermal stabilities of most of these alternative propellants address many of the handling and storage concerns posed by hydrazine-based materials. One propellant in particular—nitromethane—is already used in numerous industrial applications that include fuel additives and explosives, and it possesses a higher energy density and higher specific impulse than current hydrazine monopropellants. These useful physical properties, combined with a low material cost and widespread production, make nitromethane an ideal candidate for, at least, controlled study in a laboratory environment and a useful guide in the testing and development of hydrazine alternatives.

In the years directly after the Second World War, NAVORD conducted a series of tests to measure the burning rate of nitromethane as a function of chamber pressure [2], while a similar study was conducted two decades later by Raikova in Moscow [3]. After a period of reduced interest, the recent desire to replace toxic hydrazine has brought nitromethane back to the forefront and broadened the variety of monopropellant ignition techniques to include newer resonant lasers [4] along with the older nickel–chromium wire [5,6]. In 1999, researchers from the Pennsylvania State University measured the temperature sensitivity and intrinsic burning rate of nitromethane in a liquid-fed burner system [7]. Members from this same group also studied nitromethane combustion under static strand burner conditions [8] separately from Kelzenberg et al. in Germany [9], while Boyer from the

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Pennsylvania State University continued his work on measuring and modeling nitromethane combustion with a dissertation in 2005 [10]. These separate studies utilized chamber pressures that varied from 0.5 to 172 MPa and revealed the presence of several different pressure regimes of burning behavior from 3 to 15 MPa, 15 to 70 MPa, and 70 to 170 MPa [10]. Within each pressure range, the linear burning rate of nitromethane (r_b) is defined using the same numerical form shown in Eq. (1) with a unique empirical coefficient (a) and pressure exponent (n) [11].

$$r_b = aP^n \tag{1}$$

Many of the recent nitromethane studies were completed at chamber pressures that fell within the regime of burning behavior from 3 to 15 MPa; the pressure limits of the current study were set at similar values of 3 and 14 MPa to facilitate a direct comparison of the results herein to those gathered by previous groups [8,10].

The performance of nitromethane and other monopropellants can be enhanced through the addition of metal and metal oxide additives, increasing their usefulness through improvements in energy density and specific impulse. Advancements in the manufacture of nanoparticles have yielded a wide array of recent studies involving the combination of nano-scale particles and liquid propellants to create combustible nanofluids. The relative stability and safety of nitromethane allow researchers to concentrate solely on the tailoring of combustion behavior through this nanoparticle addition, uncovering performance trends that will guide future studies completed with more exotic monopropellants, such as EILs.

Over the past two decades, these nanofluid combustion studies have included synthesized alumina catalysts dissolved in JP-10 [12], aluminum powder mixed with water [13], and three-part mixtures of aluminum, water, and hydrogen peroxide [14]. However, the effects of nano-scale additives on the specific burning behavior of nitromethane have only entered the arena of study in more recent years. One past report by Weiser et al. examined the behavior of nitromethane gelled by Aerosil 200 fumed silica and ALEX fine aluminum particles [15]. A separate study by Sabourin et al. examined the effect of nano-scale, functionalized graphene sheets on the burning rate of nitromethane, measuring marked increases in the linear burning rates of mixed samples over those of neat nitromethane [16]. The same group returned to testing nitromethane mixtures, this time with varying concentrations of 38-nm 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 [17]. Earlier this year, a previous study by the authors chronicled the development and implementation of a pressure-based technique to estimate the linear burning rate of both liquid monopropellants and heterogeneous mixtures without the need for direct observation of the burning front [18]. This study was built on the groundwork laid in a thesis by Warren that described initial attempts to measure the linear burning rate of neat nitromethane in a similar strand burner configuration [19].

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

Presented first are details of the experiments to achieve the heterogeneous monopropellant burning rates, including the procedures for making and verifying homogeneous mixtures of liquid nitromethane and nano-sized particles and the burning rate apparatus and methods. The results of the experimental study are provided next, including relevant discussions. This section is comprised of the results for mixtures containing just silica or both silica and aluminum, followed by the results and discussion for mixtures containing a commercial titania catalyst.

2. Experimental methods

The constant-volume strand burner used in the current study can record the instantaneous chamber pressure, light intensity, and electromagnetic emission spectrum for a small sample of solid or liquid propellant throughout the combustion process. To measure burning behavior over a wide range of ambient pressures, the strand burner was pressurized to the desired conditions using compressed air. A previous study completed by the authors measured the burning rate of neat nitromethane when pressurized by various combinations of compressed air and inert argon gas, finding that the linear burning rate was unaffected by the concentration of compressed air and the oxygen inherent therein [18]. However, these same trials also revealed that nitromethane was much more difficult to reliably ignite without the presence of some ambient oxygen. These previous observations indicated that the 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 propellant mount was created to fit into the bottom of the strand burner and house each 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 propellant mount, igniting the monopropellant through resistance heating of the wire. At lower initial pressures, some mixtures became difficult to ignite and necessitated the use of a small segment of mono-modal AP/HTPB solid rocket propellant threaded onto the wire. In a previous study by the authors, the measured burning rate of nitromethane housed within a steel cavity was shown to be artificially inflated by a

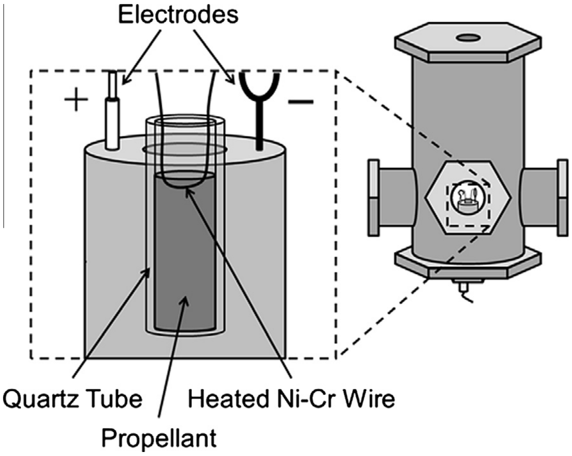

Fig. 1. Custom propellant mount used to house and ignite liquid monopropellants in the strand burner.