



Stabilized microparticle aggregates of oxygen-containing nanoparticles in kerosene for enhanced droplet combustion



Philip M. Guerieri, Rohit J. Jacob, Jeffery B. DeLisio, Miles C. Rehwoldt,
Michael R. Zachariah*

University of Maryland, College Park, MD 20740, United States

ARTICLE INFO

Article history:

Received 1 May 2017

Revised 27 June 2017

Accepted 30 August 2017

Available online 16 October 2017

Keywords:

Metal oxides

Nitrocellulose

Electrospray

Fuel additives

Droplet combustion

ABSTRACT

Metallizing and gelling hydrocarbons has received attention since the 1960s, but slurry fuels utilizing micron particles suffer from long particle burning times and problematic agglomeration. This study investigates single droplet combustion of kerosene with oxygen-containing nanoparticle additives, assembled by electrospray into nitrocellulose (NC)-bound composite “mesoparticle” (MP) structures (on the order of 5 μm). We find significantly improved dispersion properties of these materials compared to unassembled nanoparticles. Droplet combustion is characterized with a free-falling droplet experiment utilizing high speed videography. The MP pre-assembly strategy demonstrated previously by this group to improve burning rate effects and suspension stability of nanoaluminum is extended to oxygen-containing nanoparticles of CuO, KIO₄, MgO, and Al₂O₃ added to kerosene as NC-bound MPs. Burning rate enhancements of up to 40% are seen for CuO and KIO₄ MPs. Direct observation of droplet combustion disruptions is used to propose active mechanisms for each additive.

© 2017 Published by Elsevier Inc. on behalf of The Combustion Institute.

1. Introduction

The application of various propulsion methods is limited by the operating envelope of the flight vehicle and energy source utilized [1]. Air-breathing propulsion, for instance, can deliver a higher specific impulse than rockets by utilizing atmospheric oxygen instead of an on-board oxidizer, but cannot operate outside specific flight envelopes without ample oxygen delivery to the engine [1–2]. Such technological limitations on propulsion can be mitigated by modifying the combustion properties of fuels and propellants available to vehicle engineers. Namely, increasing the volumetric energy density of liquid fuels/propellants with the addition of solid particles has received attention since proposed in 1962 [3]. However, subsequent investigations examining slurry fuels of micron-sized metal powders in combustible liquids demonstrated deleterious agglomeration effects which caused low burning rates and poor combustion efficiencies [4].

Nanoscale energetic powders are known to overcome weaknesses of their micron-scale counterparts, including reducing ignition delay and increasing reaction rates by increasing the surface-to-volume ratio of the material [5]. Nanoparticles (“NPs”) are also better suited to liquid incorporation wherein Brownian motion and

repulsive electrostatic forces can prevent gravitational settling of the additives in the fluid [3]. This has prompted increased research efforts over the last decade on NPs suspended in combustible liquids. NO_x, hydrocarbon, and CO emissions can be decreased in diesel engines with NPs of Al [6–8], Al₂O₃ [7], Fe [8], B [8], CeO₂ [9], Fe₃O₄ [10], and Carbon Nanotubes (CNT) [11]. Metal oxide NPs have also been employed as oxygen carriers for direct oxidation of JP-10 in an atomized flow reactor [12]. Nanoaluminum (“nAl”) is known to reduce the ignition delay of JP-8 [13] and increase the specific impulse of JP-10 [14], and nitromethane burning rates can be increased by the addition of various nanomaterials including functionalized graphene sheets [1], silica [2,15], AlOOH [1], Al₂O₃ [15], or nAl [2,16].

Recent studies examining single-droplet combustion and evaporation of nAl-laden fuels have identified beneficial mechanisms of these additives including radiative absorption of the particles from the flame, increased heat of combustion, and physical droplet disruptions promoting mixing and secondary atomization [17–22]. However, particle agglomeration persists as a detrimental side effect of NPs in suspension [17,20,23–26]. Long-term stability can be improved with surface modification agents; e.g. trioctylphosphine oxide (TOPO), oleic acid, or sorbitol oleate [14,5,27].

Observations show that physical droplet disruptions during evaporation or combustion upon nAl addition are common and thought to disrupt agglomerate formation and inhibit shell growth [26,27]. Miglani and Basu found that higher particle loadings

* Corresponding author.

E-mail address: mrz@umd.edu (M.R. Zachariah).

suppressed gas ejections which were observed more frequently for low particle loadings, suggesting that a feedback loop exists between formation of agglomerate shells and resulting droplet disruptions that can dismantle them [26]. Including nitrocellulose (“NC”) as a gas-generating co-additive with nAl in kerosene has also been shown to promote droplet disruptions and increase burning rate constants of nAl-laden droplets [27].

We have previously reported that nitrocellulose can be used to assemble nanoparticles into porous agglomerate “mesoparticles” (MPs) on the order of 1–10 μm in size which exhibit enhanced combustion compared to nAl [28]. The strategy was extended to thermite mixtures [29] demonstrating a three-fold increase in constant volume combustion pressure rise and pressurization rate for nAl/CuO MPs compared to physical mixtures. This effect was attributed to more intimate contact of the fuel and oxidizer and gas generation by NC decomposition dispersing the reactant particles thereby mitigating reactive sintering [29]. The mechanism of primary particle dispersion to mitigate sintering and promote high burning rates was supported by aerosol-based combustion observations in [30] and MPs were employed in solid rocket propellant in [31]. This MP architecture has been used to preassemble nAl for addition to kerosene, showing significantly increased suspension stability, higher maximum stable loadings, and therefore greater maximum burning rate increases versus physical mixtures of nAl and NC nanoparticles [27]. This study evaluates effects of oxygen-containing solid particles of CuO, KIO₄, MgO, and Al₂O₃ on the single-droplet combustion of kerosene in a free-droplet configuration when the same gas-generating NC co-additive and MP preassembly strategy is employed to promote droplet disruption, agglomerate break-up, and suspension stability.

2. Experimental

2.1. Nanofuel preparation

Samples tested in this study were chosen to investigate oxide compounds of various natures: CuO, a metal oxide commonly used in thermite mixtures which thermally decomposes to release oxygen; KIO₄, a periodate salt more recently demonstrated as a strong oxidizer of reactive metals which also releases oxygen by thermal decomposition [32]; MgO, a metal oxide expected to be more stable than CuO but which has some possibility of oxidizing combustion species; and Al₂O₃, a stable metal oxide expected to be inert.

Nanopowders of CuO, MgO, and Al₂O₃ were used as-received from Sigma-Aldrich which specified <50 nm particle sizes for all three materials (Sigma-Aldrich 544868, 549649, and 544833, respectively). SEM images shown in Fig. S1 (in Supporting information) confirm primary particle sizes on the order of 50 nm, but show secondary particle agglomerate sizes of 0.5–5 μm for CuO and 1–10 μm for MgO and Al₂O₃ within tertiary fractal aggregates on the order of 50–100 μm . KIO₄ nanoparticles were synthesized by spray-drying as-received KIO₄ (Sigma-Aldrich 210056) dissolved at 4 mg/mL in deionized water from a venturi-style collision atomizer through a silica diffusion dryer into a tube furnace at 200 °C and was collected with an in-line 400 μm membrane filter [33]. Resulting particles are on the order of 0.1–1 μm primary particles in agglomerates of 0.5–10 μm . NC nanoparticles required for NC-only control samples were assembled by spray drying precursor, composed of NC collodion (Fluka Analytical 09986) diluted with acetone to approximately 25 mg/mL NC solids, into two in-line tube furnaces at 80 °C and collecting the particles in a 400 μm membrane filter heated to 90 °C to prevent solvent condensation.

Nitrocellulose-bound mesoparticles were assembled using electro-spray particle synthesis described by Wang et al. [28] wherein precursors of solid particles suspended in NC solutions (3:1 ethanol:ether solvent) are agitated in a sonication bath for 1 h

Table 1

Sample mass loadings tested by mixing with 0.3 mL of kerosene including 50 mg/mL TOPO surfactant. Control samples (not shown) included neat kerosene, kerosene with TOPO surfactant, and NC nanoparticles in kerosene/TOPO at loadings of 2–10 mg/mL. Oxygen molarity defined by the oxygen content of the oxides in the final nanofuel suspensions.

		A	B	C	D
Oxygen molarity		0.44	0.89	1.33	1.78
Sample		Mass loadings (mg/mL)			
1	CuO NPs	35.4	70.8	106.1	141.5
2	KIO ₄ NPs	25.6	51.1	76.7	102.3
3	MgO NPs	17.9	35.9	53.8	71.7
4	Al ₂ O ₃ NPs	15.1	30.2	45.3	60.5
5	CuO/NC MPs (6.4 wt% NC)	37.8	75.5	113.3	151.1
6	KIO ₄ /NC MPs (6.7 wt% NC)	27.4	54.9	82.3	109.8
7	MgO/NC MPs (7.7 wt% NC)	19.4	38.8	58.2	77.6
8	Al ₂ O ₃ /NC MPs (8.1 wt% NC)	16.4	32.9	49.3	65.8

and magnetically stirred for 24 h before injection via syringe at 2.5 mL/h through a 0.43 mm ID stainless steel probe needle charged at 10 kV, 10 cm from and perpendicular to the probe needle, an aluminum foil collection substrate is charged to –10 kV to induce fluid breakup at the needle exit into microdroplets of precursor which dry in flight before deposition on the foil.

Nanofuel suspensions are mixed by adding NPs or MPs to 0.3 mL of kerosene (Sigma-Aldrich 329460, reagent grade) with 15 mg of trioctylphosphine oxide (TOPO) surfactant, agitating by sonication bath, and magnetically stirring for approximately 24 h immediately before combustion trials. Sonication bath times were 1 h for NP suspensions and 5 min for MP suspensions to limit possible MP damage while maximizing NP aggregate disassembly and suspension. TOPO surfactant is required to chemically stabilize particles in suspension and was proposed for this purpose by E et al. to stabilize boron in JP-10 in [14] and has successfully stabilized nAl/NC MPs [27]. To simplify comparison of nanofuel burning rates using one common control, constant TOPO concentration (50 mg/mL), nanofuel batch size (0.3 mL), and mixing/storage vial size (0.5 Dr) was maintained for all samples in this study. Each sample was removed from stirring and sonicated for 1 min prior to combustion experiment trials to ensure particle dispersion. The loadings of samples tested are shown in Table 1, which were based on equal oxygen content of the additives, constant for each loading category A–D (except for NC binder-only control samples which do not include oxides). NC binder mass throughout the study is five weight percent of the theoretical reactive mixture, i.e. 5 wt% of a stoichiometric mixture of the oxygen-containing nanoparticles and nAl fuel for direct comparison with past and planned companion studies [27].

2.2. Combustion characterization

Measurements of burning rate constants were taken using a apparatus described in previous studies [34,27]. Nanofuel droplets approximately 600 μm in diameter free-fall past two methane diffusion flame igniters within a 5 × 5 × 20-in. tower filled with oxygen gas at room temperature. A magnified shadowgraph of droplets passing the igniters using an expanded HeNe laser is imaged with a high-speed camera to record initial droplet diameters (± 0.01 mm estimated uncertainty) while a second high-speed camera captures the flame emission of the droplet over its entire burning time. By assuming full combustion of the droplets (supported by product particle capture [34,27]) such that the final diameter is taken to be zero, the burning rate constant is calculated for each droplet using Eq. (1),

$$K = \frac{1 - D_{\text{Extinction}}^2/D_0^2}{t_{\text{Extinction}}/D_0^2} \cong \frac{D_0^2}{t_{\text{Extinction}}} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/4764495>

Download Persian Version:

<https://daneshyari.com/article/4764495>

[Daneshyari.com](https://daneshyari.com)