

Effects of Addition of Energetic Nanoparticles on Fuel Droplet Combustion at Dilute and Dense Particle Loading

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1 Introduction

Due to their high combustion energy, metal particles could be employed as energetic additives in propellants and explosives [1]. Due to the high specific surface area, which results in high reactivity and the potential ability to store energy on the surface, metal nanoparticles offer shortened ignitions delay, decreased burn times, more complete combustion than micron-sized particles [1, 2].

Mixing nanoscale energetic materials with traditional liquid fuels to get enhanced combustion properties is gaining increasing interest. Energetic nanoparticles can increase the volumetric heat release (or energy density) of liquid fuels and thus can potentially enhance performance of current propulsion systems. Studies on ignition and combustion behavior of liquid fuels with nanoscale additives, however, are rare. Jackson et al. [3] measured the ignition delay time of slurries of n-dodecane and nano-aluminum particles in shock tube and it was demonstrated that the addition of nano-aluminum could substantially decrease the ignition delay time under temperatures above 1175K. Decreased ignition delay time was further proved by Allen et al. [4] using a rapid compression machine. They found the ignition delays of ethanol and JP-8 were reduced by 32% and 50% respectively by seeding aluminum nano-particles. Tyagi et al. [5] investigated the effects of small quantities of aluminum and aluminum oxide nanoparticles on the ignition properties of diesel fuels using a simple hot-plate experiment. It was observed that the ignition probability for the fuel mixtures that contained nanoparticles was significantly higher than that of pure diesel. Beloni et al. [6] recently studied combustion of decane-based slurries with metallic nano additives using a lifted laminar flame burner, considering pure aluminum, mechanically alloyed $\text{Al}_{0.7}\text{Li}_{0.3}$, and nanocomposite 2B+Ti as additives. Their effects on flame length, flame speed, flame emissions and temperatures were measured. These studies have shown promise of using nanoscale additives such as energetic nanoparticles to enhance combustion of liquid fuels.

Gan and Qiao [7] recently compared the burning characteristics of fuel droplets with nano and micron-sized aluminum particles. The results show at dense loading rate five distinctive stages (preheating and ignition, classical combustion, microexplosion, surfactant flame, and aluminum droplet flame) were identified for nanosuspension, while only the first three stages occurred for micron suspension. For the same solid loading rate and surfactant concentration, the disruption and microexplosion behavior of the micron suspension occurred later with much stronger intensity. The intense droplet fragmentation was accompanied by shell rupture, which caused a massive explosion of particles, and most of them were burned during this event. On the contrary, for the nanosuspension, combustion of the large agglomerate at the later stage requires a longer time and is less complete because of formation of an oxide shell on the surface. This difference is mainly due to the different structure and characteristics of particle agglomerates formed during the early stage, which is a spherical, porous, and more-uniformly distributed aggregate for the nanosuspension, but it is a densely packed and impermeable shell for the micron suspension.

The present paper focuses on the effect of nanoparticle loading rate on droplet burning characteristics, dilute v.s. dense. Additionally, particle dynamics and suspension quality under dilute and dense loading conditions are investigated. The paper starts with fuel formulation methods including particle dispersion, de-agglomeration as well as fuel characterization. The droplet combustion experiment and diagnostic methods are then described. Most importantly, the burning behavior of fuel droplets with dense and dilute particle loadings were compared. Finally, the effects of surfactant and particles on droplet burning rate are discussed.

2 Fuel Preparation and Characterization

The methodology of physical and chemical methods to disperse the particles evenly in base fuels and to avoid agglomerate was described in our previous study [7]. Here, we will only briefly discuss the preparation process and characterization results. Two-step process [8] was adopted to prepare nanofluids-type fuels. Nanoparticles were firstly produced as a dry powder by physical or chemical methods such as inert gas condensation and chemical vapor deposition, which is followed by powder dispersion in liquid. Sonication [9] and surfactant were used to separate particles from each other, reduce agglomeration, and promote chemical stabilization of the suspension.

Two liquid fuels, n-decane and ethanol, were considered as the base fluid. Nano-Al particles (mean diameter of 80nm) were considered as additives. The particles are naturally passivated with a thin layer of Al_2O_3 (2-8 nm). Particles were mixed with liquid fuels by vigorous stirring at first and then sonicated was performed in an ice bath for about 5 minutes. With sonication, suspensions of n-decane/nano-Al (10 w.t.%) typically can remain stable for about 10 minutes, beyond which particles start to settle down. All particles settle on the bottom of the test tube after about a hour. Suspensions of ethanol/nano-Al can last for 24 hours without obvious sediment, much longer than n-decane/nano-Al. To reduce particle agglomeration, we used Sorbitan Oleate (Fig. 1) as a surfactant with its physical properties, e.g., boiling point and viscosity in Table 1 compared with the base fluids n-decane and ethanol. The maximum concentration of the surfactant was 2.5 w.t.%. With even 1 w.t.% surfactant, the n-decane/nano-Al suspension can maintain homogenous for at least 3 hours, significantly longer than the suspension without surfactant. The surfactant can stabilize the suspensions because of the steric stabilization mechanism [10], shown in Fig. 2.

Table 1 Physical property of different liquids [7]

	Chemical Formula	Molecular Weight	Boiling Point (K at 1atm)	Viscosity (mPa·s at 20°C)
n-Decane	$\text{C}_{10}\text{H}_{22}$	142	447	0.92
Ethanol	$\text{C}_2\text{H}_6\text{O}$	46	352	1.2
Sorbitan Oleate	$\text{C}_{24}\text{H}_{44}\text{O}_6$	428	852	1200-2000

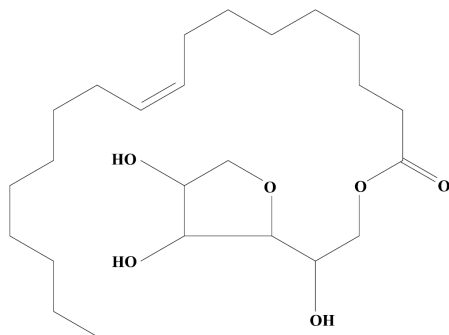


Figure 1. Chemical structure of Sorbitan Oleate.

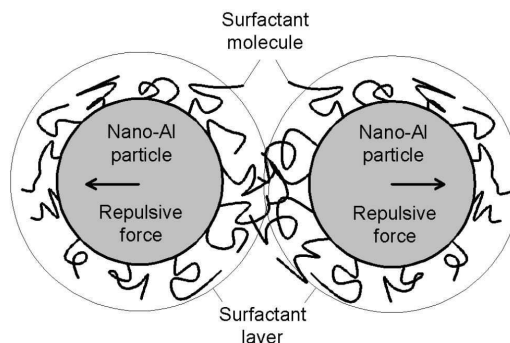


Figure 2. Schematic of steric stabilization [10]

3 Experimental Apparatus

Continue your text here. Figure 3 shows a schematic diagram of the droplet combustion experiment. The experiments were performed in a closed cylindrical stainless-steel chamber, which has four quartz windows for optical access. Two silicon carbide (Si-C) fibers with a diameter of 78 μ m were used to suspend the droplet. Droplet was produced using a syringe pump for accurate control of the size and then transferred to the cross point of silicon carbide fibers with a hypodermic needle. Si-C fiber was chosen because of its low conductivity compared to metal wires. Ignition was achieved using a heating wire located right beneath the droplet, which is made of Nickel and Chromium alloy with a resistance of about 1.5 Ω . A solenoid device was used to move the heating wire away right after the droplet was ignited.

The droplet burning process was recorded by two orthogonally located high-speed digital cameras, both with a framing rate up to 10,000 fps. One camera was for direct imaging of the flame, and the other was with backlight for better determination of droplet size and observation of droplet disruption/breakup. Images were analyzed by a Phantom image analyzing software. To measure droplet temperature history, we used a type K thermocouple made of platinum (Pt) and platinum-rhodium (Pt-Rh) wires of 75 μ m to suspend droplet, instead of using both Si-C fibers and a thermocouple to minimize the intrusive to the droplet. A 1000 Hz data acquisition system recorded the temperature history, which was synchronized with the high speed digital camera so that the droplet size and temperature history was measured simultaneously.

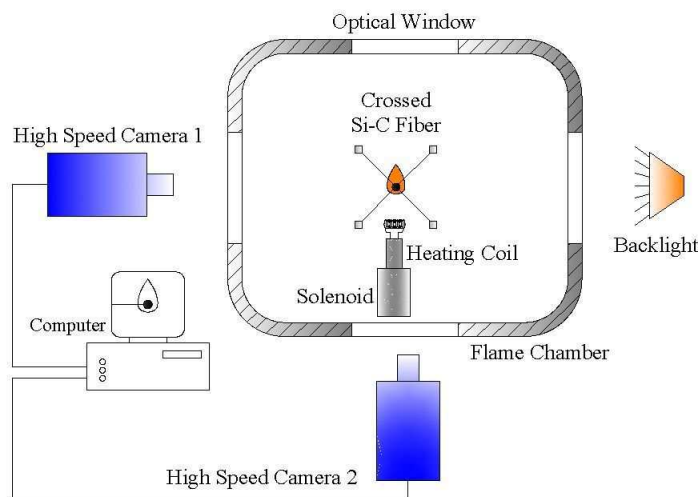


Figure 3. Schematic of the experimental setup

4 Results and Discussion

A. Droplet Combustion with Dense and Dilute Particles Loading

To understand the effect of particle loading rate, surfactant was not used for the experiments in this section to avoid the complicated burning process. Our experience shows that nanoparticles and micron particles, especially the latter, tends to settle down rather quickly in n-decane if no surfactant is added. On the contrary, using ethanol as base fluid can provide a good quality suspension even without the help of a surfactant. This is because of ethanol's higher viscosity and its ability to the formation of weak gel structures around the particles. The results shown in the following are based on ethanol as base fluid. The burning characteristics of ethanol droplets with dense (10 wt.%) and diluted (0.1 wt.%) nanoparticles were compared in Fig. 4 and Fig. 5.

For the droplet with dense (10 wt.%) particle loading, two combustion stages were identified. The droplet was ignited in Fig. 4 (a). The first stage was characterized by steady combustion of the droplet, similar to combustion of a pure ethanol droplet. Very few nanoparticles were ignited during this stage, as shown in Fig. 4 (b). The second stage started when a large agglomerate was formed on the cross point of the fibers as shown in Fig. 4 (c). After the droplet flame was extinguished, the Al agglomerate was melted into Al droplet and then an Al vapor flame was established (Fig. 4 (d)). Finally, a solid residue was left on the cross point of the fibers after Al vapor flame extinguished, as shown in Fig. 4 (e).

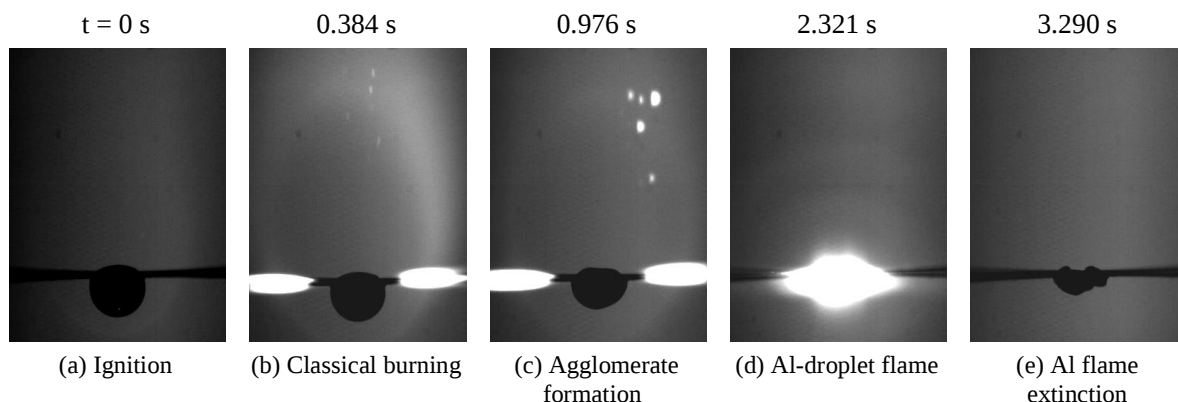


Figure 4. A burning sequence of a non-stabilized ethanol/nano-Al droplet.

The nano-Al (80 nm) concentration is 10 wt.%.

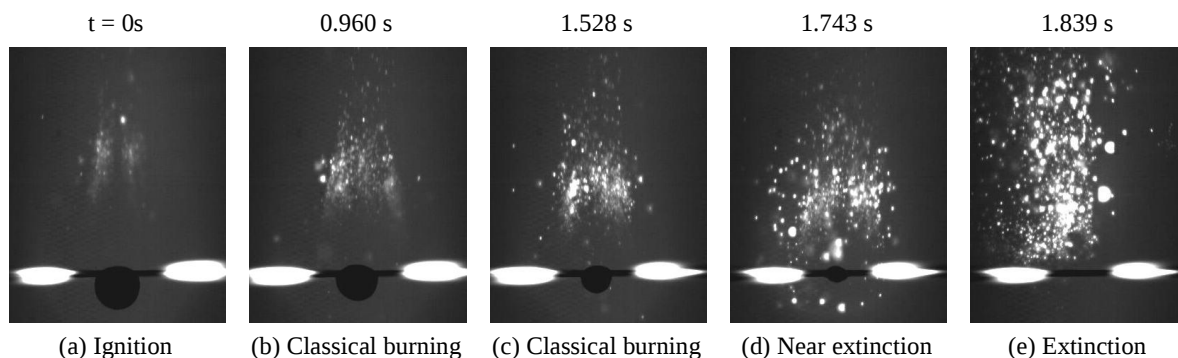


Figure 5. A burning sequence of a non-stabilized ethanol/nano-Al droplet.

The nano-Al (80 nm) concentration is 0.1 wt.%.

The burning characteristics of droplet with dilute nanoparticle loading (0.1%) are shown in Fig. 5. The burning behavior is completely different from that with dense particle loading. The droplet was burned steadily in a similar manner as a single-component droplet. However, particles were continuously transported to the hot flame zone, and then ignited and burned. We observed that nanoparticles escaped from the surface of droplet, reached the flame zone where the temperature is high and there are more oxygen. The particles were then ignited and burned, rising up due to natural convection. Thus, the ignited nanoparticles were heavily populated in the top tail of the envelope ethanol flame. Almost all nanoparticles were burned simultaneously with burning of base fuel, without forming an aggregate or leaving burned residue on the fiber, as shown in Fig. 5 (e). Additionally, as droplet size decreases, more particles were ignited and burned, comparing Fig. 5 (a), (b) & (c). This may be because shrinking of the droplet increases particle concentrations and thus more particles can escape from the droplet and reach the hot flame zone.

The different burning behavior of nanoparticles in fuel droplets under dense and dilute loading can be explained by particle transport and dynamics inside the droplet. Under dense loading (10 w.t.%), the number density of nanoparticles is higher and the collision rate for each particle is higher. Thus, particles are much easier to collide with others to form an aggregate. As the droplet surface regresses, nanoparticles and nano-agglomerate tend to move inward and form a large agglomerate on the cross point of the fibers. Because of the strong tendency of agglomeration, individual particles have little chance to transport to the droplet surface and then escape from the surface. Under dilute loading rate (0.1 w.t.%), particle number density is much lower and the collision rate for each particle is much lower. The random Brownian motion is the dominant mechanism for particle transport. Following the

outward diffusion of the liquid fuel, particles could have the chance to escape from the droplet surface as the droplet was continuously vaporized. This resulted in the observed continuous ignition and burning of particles in the area around the flame zone.

B. Effect of Particles Loading and Surfactant on Droplet Burning rate

The burning rates of three different fuels were examined to study the effect of surfactant and particles loading, and their scaled droplet size histories were shown in Fig. 6 (a). The burning rate (K) for each fuel corresponds to the slope of each straight line. Surfactant's influence on the burning characteristics has been discussed in the previous sections. Since the surfactant tends to form a thin layer around the droplet surface, the diffusion of liquid fuel inside will be somewhat inhibited. As a result, the burning rate for n-decane/surfactant ($K_2=0.550$) will be smaller than that for pure n-decane ($K_1=0.644$). For nanoparticles interior, they tend to agglomerate and a agglomerate structure will be formed inside the fuel droplet as more liquid fuel is vaporized and burned. The liquid fuel needs to diffuse out of the agglomerate structure and then the surfactant layer. The diffusion barrier due to the existence of agglomerate structure will further reduce the burning rate, which was proven by the even lower burning rate for n-decane/nano Al/surfactant ($K_3=0.474$) compared with that for n-decane/surfactant ($K_2=0.550$). The effects of particles on burning rate were further validated in Fig. 6 (b), where burning rates of stabilized droplets with varied particle loading rate (with 1%, 10% and 20% nanoparticles respectively) were compared. The inhibiting effect of particles was further confirmed by the fact that high loading rate will lead to lower burning rate.

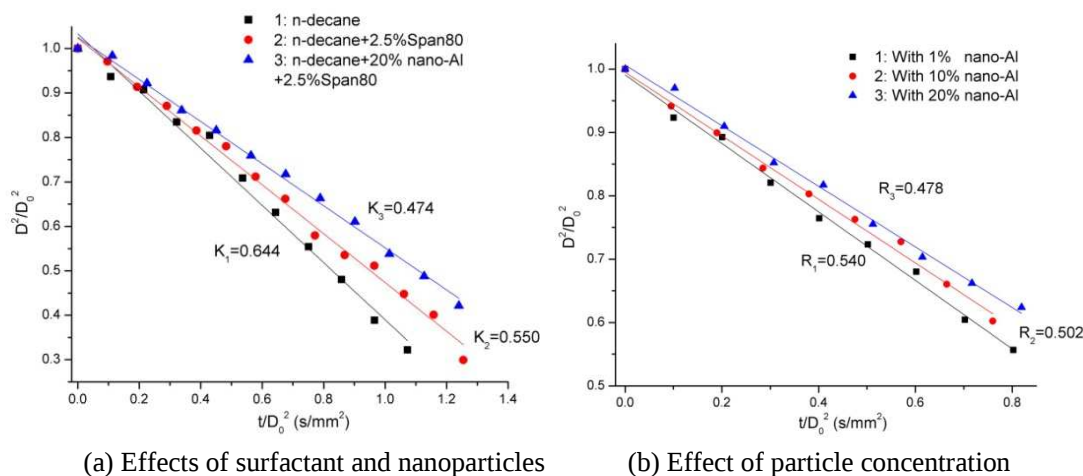


Fig. 6 Burning rates comparison of different fuels with dense particles loading

5 Conclusion

The burning characteristics of fuel droplets containing dense and dilute nanoscale aluminum particles were compared. Additionally, the effect of surfactant and particles loading on droplet burning rate were determined. It is found that ethanol/nano-Al suspension can last much longer than n-decane/nano-Al suspension. This is mainly due to the fact that ethanol tends to form a gel structure surrounding the particles making the suspension more stable. Also, ethanol has a higher viscosity than n-decane so that the particles move slower in ethanol. The results show that at high particle loading rates, nanoparticles tend to agglomerate easily. Without the presence of a surfactant, the burning process has two distinctive stages - burning of the liquid fuel droplet as the first stage and burning of the large particle aggregate as the second stage. Burning of the large particle agglomeration increases the overall burning time and may not be complete because of the oxide shell formed on the surface. At low particle loading rates, however, most particles were continuously transported to the flame zone shortly after the droplet was ignited. Most particles are burned during the burning process of the liquid droplet. Thus, low particle loading rate may be more attractive in practical applications as it can still

increase the energy density of the fuel without increasing the overall burning time. Moreover, particles can be burned more completely without forming a large agglomerate. Additionally, the suspension quality is much better at low loading rate because of much lower interparticle collision rate. Finally, addition of surfactant and solid particles slightly reduces droplet burning rate at dense loading rates. The former is because of the surfactant layer formed around the droplets that inhibit diffusion. The latter is because of a solid agglomerate formed inside the droplet which also inhibits diffusion.

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