



# Catalyzing aluminum particle reactivity with a fluorine oligomer surface coating for energy generating applications



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## ABSTRACT

Exothermic surface reaction between fluorine from a fluorine-containing polymer and the alumina ( $\text{Al}_2\text{O}_3$ ) monolayer shell surrounding aluminum (Al) fuel particles promotes aluminum reactivity. This study investigates the reactivity of Al when coated with a liquid fluorinated oligomer, specifically perfluoropolyether (PFPE). Flame speeds, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and quadrupole mass spectrometry (QMS) were performed for Al-PFPE blends with varying Al particle sizes (i.e., 80, 100, 120 and 5500 nm average diameter). The results show that the combustion performance of these blends is highly dependent on the  $\text{Al}_2\text{O}_3$  exposed surface area that catalyzes the decomposition of PFPE. As Al particle diameter increases from 80 to 120 nm, the Al-PFPE blends exhibit an increase in flame speeds by 48% and a corresponding increase in surface exothermic reaction identified as a pre-ignition reaction (PIR) that promotes an increase in the calorific output of the main reaction. But, from 120 to 5500 nm Al-PFPE blends, flame speeds decrease by 93%. The higher activation energy and lower Al- $\text{Al}_2\text{O}_3$  particle surface area to volume ratio for micrometer-scale Al fails to significantly catalyze the PIR and results in reduced overall Al reactivity. These results introduce a new and simplified synthesis approach for catalyzing a PIR in Al that strategically promotes overall Al particle reactivity.

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## 1. Introduction

Energetic blends of aluminum (Al) and fluorinated oxidizers such as polytetrafluoroethylene (PTFE) have been widely studied due to the exothermic surface reaction between fluorine (F) and the alumina shell surrounding the Al particles which promotes Al reactivity. Fluorine is more electronegative than oxygen ( $\chi_{\text{p,oxygen}} = 3.4$  and  $\chi_{\text{p,fluorine}} = 4.0$ ) [1], and the Al-F bond is one of the strongest in nature (i.e.  $664 \pm 6$  kJ/mol) [2]. When PTFE melts and dissociates, fluorine and fluorine-carbon radicals fragment. At these moderately low temperatures (300–400 °C) the alumina lattice contains vacant sites that are catalytic by nature [3–6]. In fact, alumina is well studied for its catalytic properties that are linked to the naturally occurring hydroxyl layer attached to the alumina surface under standard atmospheric conditions [3–6]. Heating weakens the hydroxyl bonding and corresponds to fragmentation of the fluorine containing species from PTFE such that the vacant sites on the alumina lattice are active for fluorine bonding and the

formation of  $\text{AlF}_3$ . The exothermic reaction has been observed by differential scanning calorimetry and associated with the identification of a small but prominent exothermic peak prior to the primary aluminum reaction [7–12]. This peak has been coined a pre-ignition reaction (PIR) whose onset temperature is dependent on particle size [8], fluorine source [10,13] and equivalence ratio [12].

Typically the aluminum oxide shell is considered dead weight in aluminum combustion because it is non-reactive and acts as a heat sink. By adding a fluorinated component (such as PTFE) the alumina shell reacts with fluorine to form  $\text{AlF}_3$  and promotes reactions at higher temperatures that improve Al reactivity and contribute to the overall calorific output of the reaction [7,8,14–16]. Kappagantula et al. [13] investigated the combustion of Al particles with surface functionalized fluorine-rich self-assembled monolayers (SAM). The SAM consisted of perfluorotetradecanoic (PFTD) acid ( $\text{C}_{14}\text{HF}_{27}\text{O}_2$ ) bonded to the aluminum native oxide shell ( $\text{Al}_2\text{O}_3$ ) [13]. Aluminum functionalized with PFTD successfully increased the reactivity of Al particles combined with  $\text{MoO}_3$ . In fact, the Al-PFTD composite particle combined with  $\text{MoO}_3$  demonstrated 86% greater flame speeds than Al +  $\text{MoO}_3$  for the same Al and  $\text{MoO}_3$  particle size. Kinetic analysis using differential scanning calorimetry (DSC) revealed the Al-F pre-ignition reaction (PIR) for the functionalized

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Al particles [11–13,10]. The PIR induced an earlier onset of the main exothermic reaction, thereby promoting Al particle reactivity.

Crouse et al. examined phosphonic acid functionalized nanometer-sized Al particles with polymerizable acrylates for Al loadings of 10, 30, 50, 60 and 70% [20]. They found that samples with Al loadings of 30, 50 and 60% experienced self-sustaining deflagration in open air with increasing energetic response (i.e., light intensity measured with a high speed camera). X-ray diffraction of the products showed that the primary product in the sample loaded with 30% Al was  $\text{AlF}_3$  because the blend was the closest to stoichiometric for fluorination. The samples with higher Al loading showed higher concentrations of  $\text{Al}_2\text{O}_3$  and aluminum carbide ( $\text{Al}_4\text{C}_3$ ) because the high Al content in these samples allowed for competitive reaction pathways (i.e., the formation of  $\text{Al}_2\text{O}_3$  and  $\text{Al}_4\text{C}_3$ ) [20].

Both of these studies provide evidence for the formation of  $\text{AlF}_3$  even with oxygen present in both SAM. Because fluorine is more electronegative than oxygen, Al–F bonding is favored on the surface of the particle as evidenced by the PIR [13,20]. However, the contribution of oxygen from the SAM to further reaction with aluminum is also important.

Another approach for coating the Al surface is to introduce a liquid fluorine-containing oligomer that wets the Al particle surface. Miller et al. [12] studied this idea using a perfluoropolyether (PFPE) oligomer as a viscous oil to wet the surface of Al particles. The motivation was to suspend nanometer-sized Al particles in a structural epoxy-based matrix. To extend the shelf life of the Al particles, they applied PFPE as a protective coating because of its thermal stability at low temperatures (up to 316 °C in an oxygen-rich environment) and potential to produce exothermic activity beyond 316 °C [12]. They studied the exothermic behavior for Al/perfluoropolyether blends of varying concentrations using differential scanning calorimetry (DSC) and found two exothermic peaks, one of which occurred at the PFPE decomposition temperature of 316 °C. This first peak was identified as a PIR. They also found the concentration that produced the highest heat of combustion was 30 wt.% Al corresponding to an equivalence ratio (ER) of 1.2 (i.e., slightly fuel rich). Others incorporated PFPE in nano-scale Al-based systems in order to assist with Al suspension in polystyrene fibers [21] and epoxy matrices [22]. Recently, McCollum et al. investigated thermal response of thermite blends mixed with varying concentrations of PFPE [23]. The addition of PFPE enhanced the reactivity of the thermite with a metal oxide that was more stable during PFPE decomposition [23].

Other particle fuels besides Al have also been investigated in combination with PFPE. For example, Rider et al. [24] performed thermal analysis on magnesium (Mg)-PFPE systems and found that the magnitude of the exothermic activity was highly dependent on the Mg particle surface area to volume ratio (i.e., the specific surface area). Magnesium particles sized at 1–11, <44 and 44–75  $\mu\text{m}$  produced decreasing exotherms of 9.2, 4.2 and 2.3 kJ/g with increasing particle size, respectively [24].

Others have shown a similar specific surface area affect. For example, Dean et al. analyzed DSC data for different  $\text{Al}_2\text{O}_3$  particle sizes with PTFE in order to understand the role of exposed surface area on the exothermic Al–F reaction [8]. They found that the onset

and magnitude of the PIR varied with particle size and exposed surface area for  $\text{Al}_2\text{O}_3$  average particle sizes of 15, 30, 40 and 50 nm. They observed a decrease in PIR magnitude as  $\text{Al}_2\text{O}_3$  particle size decreased from 50 to 30 nm and an increase in magnitude at 15 nm. Their results suggest an optimum Al particle diameter for promoting the Al–F surface exothermic chemistry is about 50 nm.

All of these studies [7,8,10,11,13,21,22,25,26] highlight Al–F reactions are: (1) exothermic; (2) a function of exposed  $\text{Al}_2\text{O}_3$  surface area; (3) a function of the fluorine source (i.e., PFTD, PTFE); and (4) can catalyze Al reactivity with a PIR that promotes the main Al exothermic reaction. The objective of this study is to synthesize Al-PFPE formulations on a larger scale and analyze the macroscopic combustion characteristics of the Al-PFPE reaction. This study extends the work by Kettwich, Iacono, et al. [12] who examined small (i.e. 5 mg) Al-PFPE samples for thermal equilibrium studies. All blends were prepared for a constant ER ( $\Phi = 1.2$ ). Flame speeds, DSC, thermogravimetric analysis (TGA), and quadruple mass spectrometry (QMS) were performed and analyzed for all blends in order to characterize combustion dynamics and reactivity. By coating Al particles with PFPE, surface reactions promote decomposition of PFPE and reactivity of Al. These findings have implications for the development of new applications for Al powder reactions in areas including fuel cells [27], batteries [28–30], hydrogen production [31], green and other energy generating and sustainable materials [28,31,32].

## 2. Experimental

### 2.1. Materials

Four different Al powders were studied with physical properties summarized in Table 1. The 80 and 120 nm average diameter Al particles were procured from Nanotechnologies (Houston, TX), the 100 nm average diameter Al was from U.S. Nanomaterials (Houston, TX) and the 5500 nm average diameter Al from Alfa Aesar (Ward Hill, MA). The PFPE (Fomblin<sup>®</sup> Y LVAC 25/6, average molecular weight of 3300 g mol<sup>-1</sup>) was purchased from Sigma-Aldrich (St. Louis, MO).

Images obtained for 80, 100 and 120 nm Al particles by transmission electron microscopy (TEM) using a Hitachi H-8100 TEM are shown in Fig. 1. Each spherical particle is passivated by an approximately 3.7 nm thick alumina shell as characterized by TEM analysis (Fig. 1). Due to thickness limitations with TEM, the micron-scale particles could not be measured in this way. Instead, their size was examined using an AccuSizer 780 optical particle size analyzer (Santa Barbara, CA). Particle diameter was calculated and plotted as a count-based measurement and the distribution is shown in Fig. 2 with size data given in Table 1. The oxide thickness used for purity calculations was estimated at 3.7 nm and constant for all Al powders studied here.

### 2.2. Stoichiometry

Equivalence ratio (ER) of 1.2 (i.e., slightly fuel rich) was maintained for all samples. An equivalence ratio is the balance for

**Table 1**  
Material specifications for Al fuel particles.

Al diameter (nm)	Measured particle size (nm)	Oxide layer thickness (nm)	Particle mass alumina (%)	TMD (g/cm <sup>3</sup> )	Bulk Density (g/cm <sup>3</sup> )	%TMD (%)	Specific Surface Area (1/cm)
80	76	3.9	36%	2.3	2.00	92	$7.9 \times 10^5$
100	91	3.6	29%	2.2	1.96	92	$6.7 \times 10^5$
120	121	3.6	23%	2.2	1.93	91	$5.0 \times 10^5$
5500	5800	3.7	0.6%	2.1	1.78	87	$1.2 \times 10^4$

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