The Impact of High Particles Concentration in a Biofuel Droplet Combustion

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Abstract

Aviation is one of the largest transportation sectors and is operated on fossil fuels, being responsible for about 2% of global CO_2 emissions. In order to reduce the environmental impact, biofuels emerged as a promising solution. Additionally, a possible approach to improve the performance of biofuels is to add nanoparticles, leading to the concept of nanofuel. The present work evaluates the nanofuel droplet combustion of a biofuel containing high aluminum particle concentrations. To enhance the nanofuel stability, a preliminary study focusing on the addition of a surfactant was mandatory. Particle size of 40 nm and three particle concentrations from 1.0 to 4.0 wt.% were considered. The results show that the oleic acid effectively improves the stability, and no visible oxidation of the nanoparticles was reported. Regarding the single droplet combustion, the observations show that the addition of nanoparticles promotes micro-explosions, contrary to the combustion of pure biofuel, and increases the overall droplet burning rate.

Keywords

Aluminum nanoparticles, surfactant, drop tube furnace, single droplet experiments, nanofuel

Introduction

Air transportation has been at the core of global economic growth and social development. The exclusive reliance on fossil fuels makes the aviation sector responsible for about 2% of global CO_2 emissions [1]. The continuous growth of this sector, alongside the environmental issues and the depletion of fossil fuels, has promoted the search for alternative, reliable, and sustainable energy sources that could supply aircraft. Consequently, biofuels have been studied as alternative jet fuels [2, 3].

Biofuels are a renewable energy source derived from sustainable feedstock. They promote cleaner combustion and are potentially carbon neutral. Most of the CO_2 released during their burning has been previously captured by the plants from which biofuels originated, while these were growing. Although biofuels are favorable for the environment, some drawbacks include low energy content, high viscosity, lower volatility properties, and high production costs [4]. A promising biofuel candidate to replace jet fuel in aircraft operation is the hydrotreated vegetable oil (HVO). This renewable fuel, commonly referred to as green diesel, is a paraffinic bio-based liquid obtained from hydroprocessed esters and fatty acids (HEFA). It offers higher energy density when compared to the majority of the other biofuels and promotes a significant reduction in greenhouse gases and others pollutants emissions [4, 5].

In order to improve the combustion performance of biofuels, one of the strategies is to apply fuel additives in liquid biofuels [6]. A possible approach is to disperse energetic metal nanoparticles into conventional liquid fuels. This new class of fuels is referred to as nanofluid fuels or nanofuels. The addition of metallic nanoparticles to liquid fuels brings several advantages, such as increasing volumetric energy density, enhancing the catalytic activity, lower ignition

delay, higher ignition probability, higher volumetric heat release rates, and faster ignition probability burning rates, among others [4].

Nanofuels combine the high specific surface area of nanoparticles and the high oxidation energy of metals to produce high energy density fuels, improving fuel economy and reducing pollutant emissions [7]. However, nanofuels may have some inconveniences when it comes to emissions from the combustion of solid particles and the long-term stability of the suspensions, requiring more investigations in this field. The addition of particles to liquid fuels does not present a novel subject. It has been a common practice for many years to mix micron-sized particles with fluids. However, suspending nanoparticles in conventional fluids has several advantages compared to suspending micron-sized particles. The nanoparticles include better dispersion stability, higher thermal conductivity, lower viscosity, lower pressure drop, and lower erosion [8, 9]. Numerous studies have been developed to understand the fundamentals based on the nanofuel single droplet combustion [10, 11, 12, 13, 14]. Tyagi et al. [10] noticed that the ignition probability of diesel increase when nanoparticles are added. Gan and Qiao [11] conducted a study to evaluate single droplet combustion using aluminum particles stably suspended in ethanol and n-decane. The results reveal that nanosuspensions remain stable for a much longer than micron suspensions. In addition, micro-explosion behavior occurred and was more intense for higher particle sizes. Similar to the previous work, Gan et al. [12] studied the effect of boron and iron nanoparticles in ethanol and n-decane. The addition of these particles in dilute and dense concentrations was investigated, presenting differences in droplet combustion.

In this context, the present work evaluates the effect of high particle concentrations on the combustion behavior of HVO, an alternative jet fuel. To accomplish this, the surfactant is added in nanofuels and a stability study is performed. Therefore, single droplet combustion experiments are carried out in a drop tube furnace (DTF) under two furnace temperatures $T = 800\ ^{\circ}$C and $T = 1000\ ^{\circ}$C. In addition, disruptive burning phenomena are addressed.

Material and Methods

Hydrotreated vegetable oil (HVO) is a renewable fuel, a mixture of straight-chain and branched alkanes. This alternative jet fuel is a NExBTL from NESTE that presents a high cetane number and does not contain sulfur, aromatics, and oxygen in its composition. These fuels are stable for storage, resistant to microbial growth, and do not form deposits in engines [15]. This liquid biofuel was used as the base fluid for the nanofuel. The properties of HVO are displayed in Table 1. Aluminum was chosen from the suitable candidates for hydrocarbon additives due to its energy content, abundance, and relatively low production cost. Thus, spherical aluminum nanoparticles, 99.995% pure, metal basis, with an average diameter of 40 nm, were purchased from Nanografi. In a previous study [4], the highest particle concentration tested was 1.0 wt.%. This specific value is due to the poor nanofuel stability reported for higher particle concentrations (> 1.0 wt.%). Consequently, to increase the dispersion stability of nanofuels and to allow the study of higher particle concentrations, the addition of surfactant was required. In this work, oleic acid (OA) pure, pharma grade, procured from PanReac AppliChem ITW Reagents was selected for the chemical stabilization of aluminum nanoparticles in HVO. It is also important to mention that pure HVO and HVO + OA were also tested for comparison purposes. The preparation of HVO + OA was straightforward. OA was first added to HVO on a weighing scale to obtain the desired mass fraction of each liquid. Then, the fuel blend was vigorously mixed for 10 min using a magnetic stirrer.

Regarding nanofuel preparation, a precise and appropriate procedure should be executed. The purpose is to obtain a nanofuel stable with a low level of agglomeration. Nanofuels were prepared with a two-step method. To obtain the desired particle concentrations, aluminum nanoparticles were first added to HVO on a weighing scale. Subsequently, the mixture was vigorously stirred for 20 min using a magnetic stirrer. The next step involved sonication. A probe sonicator UP200Ht, manufactured by Hielscher, was used to suspend the nanoparticles

and to breakdown the agglomerates.

Table 1. HVO properties adapted from [15].

Parameter	Standard Limit	HVO
Density (kg/m^3) (at 20 °C)	771–836	780.6
Kinematic viscosity (mm^2/s) (at 25 °C)		4.33
Surface tension (N/m) (at 20 °C)		0.0265
Final boiling point (°C)	Max. 300	308
Sulfur (wt.%)	Max. 30.0	0.09
Aromatics (wt.%)	Max. 25.0 (vol.%)	0
Lower heating value (MJ/kg)	Min. 42.8	43.9
H/C ratio		2.18
Carbon number		C15–C18

The nanofuels were sonicated in an ice bath to maintain a constant temperature, avoiding overheating resulting from continuous sonication. According to the literature, it was unclear whether the addition of surfactant should be done before or after sonication as well as the sonication parameters. Motivated by this, surfactant-to-nanoparticle mass ratio, amplitude, and sonication duration were evaluated. The observations demonstrated that by employing a sonication amplitude of 40% for 30 min and adding OA in a surfactant to - nanoparticle ratio of 1:1, it was possible to obtain stable nanofuels for at least four hours. Consequently, after the sonication, the oleic acid was added to the nanofuel. Then, the mixture was vigorously stirred for an additional 10 min using a magnetic stirrer.

Following the nanofuel preparation, the stability was evaluated for several hours and days by visual inspection. Figure 1 shows the results of the qualitative stability analysis. Based on the visual inspection, four samples levels were considered. Level A corresponds to a stable nanofuel with no evident sedimentation.
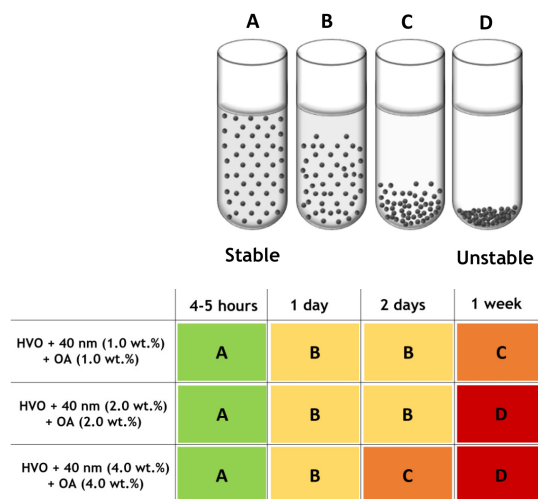

	4-5 hours	1 day	2 days	1 week
HVO + 40 nm (1.0 wt.%) + OA (1.0 wt.%)	A	B	B	C
HVO + 40 nm (2.0 wt.%) + OA (2.0 wt.%)	A	B	B	D
HVO + 40 nm (4.0 wt.%) + OA (4.0 wt.%)	A	B	C	D

Figure 1. Qualitatively stability study.

Level B and C reflect two intermediate cases, when the nanofuel is partially and highly sedimented, respectively, and level D indicates an unstable nanofuel when all the nanoparticles remain at the bottom of the test tube. As can be observed in Figure 1, the highest particle concentration studied in the present work was 4.0 wt.%. During 4-5 hours after the preparation, the nanofuel remains stable, allowing for single droplet combustion experiments to be performed with no stability issues. However, as time evolves, the stability reduces, and it is no longer possible to use the nanofuel for experimental purposes. It should be noted that more investigations

focusing on nanofuel stability must be performed to understand and introduce this novel class of fuel in practical systems.

To better understand the effect of aluminum nanoparticles in a biofuel, the nanofuel physical properties were measured. Table 1 shows the fuels properties. The density was measured with a portable density/specific gravity meter DA-130N (Kyoto Electronics Manufacturing) and the viscosity with a rheometer (TA instruments ARI 500 ex) at ambient temperature with an accuracy of ± 5%. The surface tension was determined through the pendant drop method using an optical tensiometer THETA (Attension). The measurements show that density and surface tension are not significantly influenced by the addition of particles and surfactant (< 5%). On the contrary, the viscosity presents a considerable increase when nanoparticles and surfactant are added to the HVO.

Table 2. Physical properties of fuels.

Fuels	Density (kg/m³)	Surface tension (mN/m)	Viscosity (mPa.s)
HVO	776 ± 1	26.74 ± 0.05	3.41 ± 0.02
HVO + 1% OA	778 ± 1	26.79 ± 0.05	3.48 ± 0.02
HVO + 2% OA	778 ± 1	26.82 ± 0.05	3.52 ± 0.02
HVO + 4% OA	780 ± 1	26.92 ± 0.06	3.71 ± 0.01
HVO + 1% OA + 1% Al	782 ± 1	27.01 ± 0.07	3.56 ± 0.02
HVO + 2% OA + 2% Al	788 ± 1	27.22 ± 0.07	3.70 ± 0.03
HVO + 4% OA+ 4% Al	802 ± 1	27.55 ± 0.11	4.11 ± 0.04

Regarding the single droplet combustion, the experiments were performed in a drop tube furnace (DTF) under two furnace temperature $T = 800$ °C and $T = 1000$ °C. The injection system was placed at the top of it, releasing droplets with an initial diameter of 250 ± 12 μm. The single droplet combustion setup was already employed in previous works, and a more detailed description can be found in [4, 15].

Results and Discussion

In order to properly investigate the effects of adding aluminum nanoparticles to HVO, it is important to evaluate the combustion characteristics of pure HVO and HVO + 4% OA droplets as a baseline for comparison. Figure 2 depicts the normalized diameter squared as a function of time for the two different temperatures studied. The curves were obtained by analyzing a minimum of 40 droplets, as previously mentioned by [4]. In this context, Figure 2 shows the droplet size evolution for pure HVO, HVO + 4% OA and nanofuels. As can be noticed, the droplet size evolution of pure HVO and HVO with the addition of 4.0 wt.% of OA are in accordance with the d^2-law without the existence of disruptive behavior phenomena. In addition, HVO + 4% OA practically overlaps with the temporal history of the diameter squared of pure HVO for both furnace temperatures.

Regarding nanofuel droplet combustion, all the nanofuels studied presented a similar droplet size evolution, regardless of the nanoparticle concentration. As can be observed, adding aluminum nanoparticles to HVO results in a departure from the d^2-law, emerging a new combustion phase different from the steady-state phase (where the square of droplet diameter reduces linearly with time). This was termed as the dry-out phase [4] and it is characterized by a significant decrease of the burning rate in the later stages of the droplet lifetime. Dry-out phase is caused by the agglomeration of particles near the droplet surface, which at some point in time create a resistance to the evaporation of liquid fuel. This subsequently leads to a decrease in the reduction rate of the droplet diameter, being affected by the ambient temperature. According to the literature, the tendency of the droplet size evolution curves for the nanofuels are also affected by droplet radiation absorption. Due to this, it has been hypothesized that for a concentration of 1.0 wt.% the droplet already absorbs all the incoming radiation energy, and so increasing

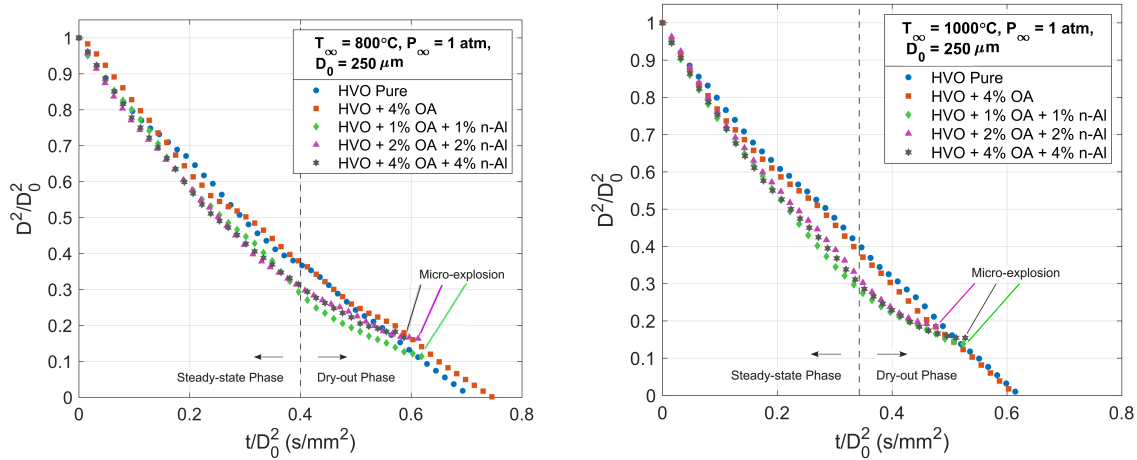the number of nanoparticles inside the droplet will not produce any noticeable improvement, as noticed in Figure 2.

Figure 2. Droplet size evolution of pure HVO, HVO with the addition of 4.0 wt.% of OA and the different nanofuels studied for: (a) $T = 800\ °C$. (b) $T = 1000\ °C$.

The addition of aluminum nanoparticles to HVO also promotes the occurrence of disruptive burning phenomena. The nanofuels studied exhibited micro-explosions with an occurrence rate of 100% at the end of their lifetime, regardless of the experimental conditions and particle concentration. These micro-explosions are responsible for significantly shortening the droplet lifetime. Figure 3 shows the disruptive burning phenomena present in nanofuel droplet combustion. A micro-explosion can be detected in the last frames in Figure 3.
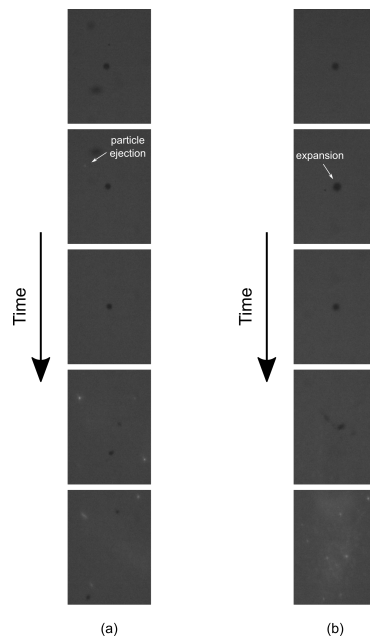

Figure 3. Events observed prior to the occurrence of micro-explosions: (a) Particle ejection. (b) Droplet expansion. The sequential frames shown in each set are separated by a time interval of 2 ms.

While evaporation occurs, the liquid fuel is being consumed, and the droplet surface is receding rapidly, sweeping in the nanoparticles that remain inside the droplet. This promotes particle agglomeration near the surface, consequently leading to the occurrence of micro-explosions and the primary droplet disintegration. Finally, the ejection of bright spots in several directions is noticed due to the aluminum combustion. As can be observed in Figure 3, two different types of disruption preceded the micro-explosions, namely (a) particle ejection and (b) droplet expansion. The former was the most commonly observed, where a small cluster of nanoparticles

was expelled from the main droplet, igniting immediately and turning into bright spots. Droplet expansion prior to its explosion was experienced several times, in which a significant and temporary increase in droplet size was registered. It should be mentioned that these two types of disruption were found to be independent of the experimental conditions, as they were noticed for each particle concentration and ambient temperature.

After comparing pure HVO, HVO + 4% OA, and nanofuels, in terms of droplet size evolution and disruptive burning phenomena, it is essential to evaluate the burning rate for all the operating conditions. Figure 4 shows the average burning rate for all the fuels tested in the present work. In order to correctly investigate the droplet burning rate, the dry-out phase was disregarded since pure HVO and HVO + 4% OA and it is only displayed the steady-state phase in the experimental results. The results reveal that the improvement in the burning rate is more significant for higher furnace temperatures. It makes sense, since for higher temperatures, more radiation energy is transmitted from the DTF walls. Moreover, pure HVO presents a lower average burning rate.
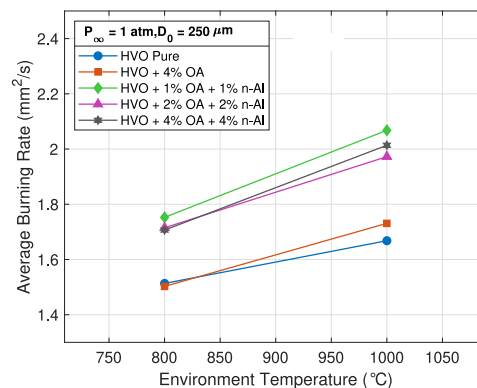

Figure 4. Average droplet burning rate for the steady-state combustion phase ($D^2/D_0^2 > 0.3$) of pure HVO, HVO with the addition of 4.0 wt.% of OA and the different nanofuels studied as a function of the furnace temperature.

Conclusions

The conclusions of this study are summarized as follows. It was found that the droplet combustion of both pure HVO and HVO with the addition of 4.0 wt.% of OA is in good agreement with the d^2-law. Furthermore, the addition of such a concentration of OA went almost unnoticed on the combustion characteristics of HVO. Nevertheless, the addition of OA substantially increased the stability of the nanofuels.

The addition of aluminum nanoparticles to HVO increased the overall droplet burning rate, which was more pronounced for higher ambient temperatures. However, the increase in the overall droplet burning rate showed no particular dependence on particle concentration for the investigated range.

Finally, the addition of aluminum nanoparticles also prompted the occurrence of micro-explosions, significantly reducing the droplet lifetime.

Acknowledgements

Nomenclature

Al Aluminum nanoparticle
DTF Drop tube furnace
$HEFA$ Hydroprocessed esters and fatty acids
HVO Hydrotreated vegetable oil
OA Oleic acid

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